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ON THE NATURE AND STRUCTURE OF THE DOUBLE HALIDES.

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In studying modern chemical literature, one cannot fail to be impressed by the fact that the compounds commonly called double salts of the halogens or double halides are generally treated, if treated at all, in a highly unsatisfactory way. Few of them are mentioned, and these are passed over as lightly as possible, but little attempt being made to explain them, or to point out the relations which exist between them and other chemical compounds. Some time ago, while engaged in the preparation of one of my text-books, I made a systematic study of the present state of our knowledge concerning these compounds, and soon reached the conviction that they are simpler than they are commonly held to be. What appears to me to be an entirely satisfactory explanation of them suggested itself; and further investigation showed that the same explanation had already been offered by others. But owing partly, I think, to the fact that the evidence in favor of the explanation has never been fully presented to chemists, it has not been generally accepted. It therefore seems to me desirable to discuss somewhat fully the facts known concerning the formation and existence of the compounds in question. I cannot but believe that a careful consideration of these facts, and of the thoughts which they suggest, will lead to the general acceptance of a conception which hitherto has received but scant recognition.

1. *Number and Formation.*

About four hundred compounds belonging to the general class of double halides have been described, and judging by the great variety of these, it would probably be a comparatively simple matter to add largely to their number, if there were any incentive to their preparation. By far the largest number of those known are formed by the direct combination of a halogen salt of one of the alkali metals with the corresponding salt of some other metal, especially aluminium, chromium, lead, platinum, etc. Many are made by bringing the halogen salts together in strong acid solution; others, like aluminium potassium chloride, $KAlCl_4$ or $AlCl_3.KCl$, by bringing the vapor of one in contact with the other salt in highly heated condition. The corresponding sodium aluminium chloride is, further, manufactured on the large scale by passing chlorine over a highly heated mixture of aluminic oxide, charcoal, and sodium chloride, *when the double salt,* $AlCl_3.NaCl$ or $NaAlCl_4$ *distills over*. Not only do the halogen salts of the metallic or basic elements combine with those of the alkali metals; the halogen compounds of the acidic elements such as sulphur, selenium and tellurium, phosphorus, arsenic, and antimony, silicon, and boron, also combine with the halogen salts of metals. But, just as the halogen compounds of the acidic elements are easily decomposed by water, so also the double salts into which these compounds enter are for the most part easily decomposed by the same agent, so that there are serious difficulties in the way of preparing such compounds in pure condition. Still, a sufficient number has been made to show that the halogen compounds of the acidic elements combine with facility with halogen salts. The evidence appears to show that under proper conditions chlorides combine with chlorides, bromides with bromides, iodides with iodides, and fluorides with fluorides, as readily as oxides combine with oxides, and sulphides with sulphides. Further, it has been shown that *mixed double halides* can be formed. Thus, when antimony trichloride, $SbCl_3$, is brought together with potassium bromide, the salt $SbCl_3.3KBr$ is formed, and there are some other examples of the same kind known, though the number is small. The chief difficulty encountered in making salts of this kind is found in the fact that they must be made in the presence of one of the halogen acids, and this at once exerts

an influence on the course of the reaction. For example, in most cases it is impossible to make a double salt containing both bromine and chlorine in a solution containing hydrochloric acid, as the bromide, under the circumstances, is converted into the corresponding chloride, and the double salt formed contains only chlorine.

There are then two difficulties in the way of preparing double halide salts. The first is the ease with which most such compounds are decomposed by water. The second is the ease with which the salt of one halogen is decomposed by the acid of another.

2. *Composition.*

A study of the double halides with reference to their composition reveals an interesting regularity which appears to be of the highest importance in enabling us to judge of their nature. The character of this regularity will be made clear by a consideration of some typical examples. There are few, if any, examples of such salts in which only univalent metals enter. Potassium chloride does not unite with sodium chloride to form a stable compound. Passing, however, to the bivalent metals as magnesium, zinc, beryllium, mercury, copper, lead, tin, etc., we find that their halogen salts form two classes of compounds represented by the following general formulas, in which M^{II} represents a bivalent metal, Hl any halogen, and M^{I} a univalent metal, generally potassium or sodium:

(1) $M^{II}Hl_3.M^{I}Hl$ or $M^{I}M^{II}Hl_3$,
and (2) $M^{II}Hl_2.2M^{I}Hl$ or $M^{I}_2M^{II}Hl_4$.

Examples of these two classes are the salts represented by the following formulas:

First Class.	Second Class.
$BeF_2.KF$ ($KBeF_3$)	$BeF_2.2KF$ (K_2BeF_4)
$MgCl_2.KCl$ ($KMgCl_3$)	$MgCl_2.2KCl$ (K_2MgCl_4)
$MgBr_2.KBr$ ($KMgBr_3$)	
$MgI_2.KI$ ($KMgI_3$)	
$ZnCl_2.KCl$ ($KZnCl_3$)	$ZnCl_2.2KCl$ (K_2ZnCl_4)
	$ZnCl_2.MgCl_2$ ($MgZnCl_4$)
$HgCl_2.RbCl$ ($RbHgCl_3$)	$HgCl_2.2RbCl$ (Rb_2HgCl_4)
$HgBr_2.KBr$ ($KHgBr_3$)	
$HgI_2.KI$ ($KHgI_3$)	$HgI_2.2KI$ (K_2HgI_4)
$SnCl_2.KCl$ ($KSnCl_3$)	

First Class.	Second Class.
$PbI_2.KI$ ($KPbI_3$)	$PbI_2.2KI$ (K_2PbI_4)
$PdCl_2.KCl$ ($KPdCl_3$)	$PdCl_2.2CsCl$ (Cs_2PdCl_4)
$PtCl_2.RbCl$ ($RbPtCl_3$)	$PtCl_2.2CsCl$ (Cs_2PtCl_4)

The halogen salts of the trivalent elements, as aluminium, iron, antimony, gold, chromium, etc., form three classes of compounds which are represented by the general formulas

(1) $M^{III}Hl_3.M^{I}Hl$ or $M^{I}M^{III}Hl_4$
(2) $M^{III}Hl_3.2M^{I}Hl$ or $M^{I}_2M^{III}Hl_5$
and (3) $M^{III}Hl_3.3M^{I}Hl$ or $M^{I}_3M^{III}Hl_6$.

Examples of these three classes are the salts represented by the following formulas:

First Class.	Second Class.	Third Class.
$BF_3.KF$	$AlF_3.2NaF$	$AlF_3.3NaF$
(KBF_4)	(Na_2AlF_5)	(Na_3AlF_6)
$AlCl_3.KCl$	$BiCl_3.2KCl$	$BiCl_3.3KCl$
($KAlCl_4$)	(K_2BiCl_5)	(K_3BiCl_6)
$AuCl_3.KCl$	$BiI_3.2KI$	$BiCl_3.3NaCl$
($KAuCl_4$)	(K_2BiI_5)	(Na_3BiCl_6)
$AlBr_3.KBr$	$CrCl_3.2KCl$	$CrCl_3.3KCl$
($KAlBr_4$)	(K_2CrCl_5)	(K_3CrCl_6)
$AuBr_3.KBr$	$SbCl_3.2KCl$	$InCl_3.3KCl$
($KAuBr_4$)	(K_2SbCl_5)	(K_3InCl_6)
$CrCl_3.KCl$	$SbF_3.2KF$	$RhCl_3.3KCl$
($KCrCl_4$)	(K_2SbF_5)	(K_3RhCl_6)
$FeCl_3.KCl$	$RhCl_3.2KCl$	$SbF_3.3KF$
($KFeCl_4$)	(K_2RhCl_5)	(K_3SbF_6)

Most of the double halides formed by quadrivalent elements have the general formula

$$M^{IV}Hl_4.2M^{I}Hl \text{ or } M^{I}_2M^{IV}Hl_6.$$

This is shown in the salts represented by the following formulas:

$PtCl_4.2KCl$ (K_2PtCl_6)
$SiF_4.2KF$ (K_2SiF_6)
$PdCl_4.2KCl$ (K_2PdCl_6)
$PtI_4.2NaI$ (Na_2PtI_6)
$PtBr_4.2NaBr$ (Na_2PtBr_6)
$SnCl_4.2NaCl$ (Na_2SnCl_6)

$TiF_4.2KF$ (K_2TiF_6)
$ZrF_4.2KF$ (K_2ZrF_6)
$GeF_4.2KF$ (K_2GeF_6)

There are a few examples of another class of double halides derived from the halogen salts of quadrivalent elements. These have the general formula

$$M^{IV}Hl_4.M^{I}Hl \text{ or } M^{I}M^{IV}Hl_5.$$

Such are the following:

$SnF_4.KF$ ($KSnF_5$)
$SnF_4.LiF$ ($LiSnF_5$)
$SiF_4.LiF$ ($LiSiF_5$)
$SiF_4.AgF$ ($AgSiF_5$)
$SnF_4.NaF$ ($NaSnF_5$)

And finally there is one representative of another class of the general formula

$$M^{IV}Hl_4.3M^{I}Hl \text{ or } M^{I}_3M^{IV}Hl_7.$$

This is the salt $ZrF_4.3KF$ or K_3ZrF_7.
Salts of the general formula

$$M^{IV}Hl_4.4M^{I}Hl \text{ or } M^{I}_4M^{IV}Hl_8$$

have not been described.

Passing to the quinquivalent elements, there are found a few representatives of five classes of compounds of the following general formulas:

$M^{V}Hl_5$. $M^{I}Hl$ or $M^{I}M^{V}Hl_6$
$M^{V}Hl_5.2M^{I}Hl$ or $M^{I}_2M^{V}Hl_7$
$M^{V}Hl_5.3M^{I}Hl$ or $M^{I}_3M^{V}Hl_8$
$M^{V}Hl_5.4M^{I}Hl$ or $M^{I}_4M^{V}Hl_9$
$M^{V}Hl_5.5M^{I}Hl$ or $M^{I}_5M^{V}Hl_{10}$.

Only two or three examples of the last two classes are known, and these have a somewhat more complicated composition than that represented by the formulas given. The substances in question are:

$AsF_5.KF$ or $KAsF_6$
$AsF_5.2KF$ or K_2AsF_7
$NbF_5.2KF$ or K_2NbF_7
$NbF_5.3KF$ or K_3NbF_8

$PCl_5.AlCl_3$ or $AlPCl_8$
$PCl_5.2SnCl_2$ or Sn_2PCl_9
$PCl_5.SbCl_5$ or $SbPCl_{10}$.

The examples given in the above tables are fair representatives of the whole class of double halides, except that all ammonium salts are omitted. The double halides formed with halogen salts of ammonium are very numerous, and many of them are quite complicated. There are indeed ammonium salts known belonging to all the classes above mentioned, but there are many others which do not belong to these classes. Considering the power of ammonium salts in general to form complex compounds with metallic salts, one cannot avoid the conclusion that there is some power in nitrogen which makes the formation of these compounds possible. The position of the double halides containing ammonium is certainly exceptional. They seem to be governed by some law of their own. As regards all other double halides, however, the examples chosen are representative. While most of these salts consist of some other halide combined with a halide of an alkali metal, there are those in which, instead of the alkali salt, a salt of calcium, barium, or, in exceptional cases, of some less strongly marked basic element, enters. Such, for example, are the following:

$ZnCl_2.BaCl_2$ or $BaZnCl_4$
$AlF_3.CaF_2$ or $CaAlF_5$
$PtCl_4.BaCl_2$ or $BaPtCl_6$
$PtBr_4.PbBr_2$ or $PbPtBr_6$
$SiF_4.CaF_2$ or $CaSiF_6$.

As will be seen, however, all these salts follow the same law of composition as those which are formed by the halides of the alkali metals. This law may be stated thus:

When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater and is generally less than the number of halogen atoms contained in the latter.

According to this law, double halides of the following general formulas are possible:

$$
\begin{array}{llll}
M^{III}\left\{\begin{array}{l}HI\\HI.M'HI\end{array}\right. & M^{III}\left\{\begin{array}{l}HI.M'HI\\HI.M'HI\end{array}\right. & & \\
M^{III}\left\{\begin{array}{l}HI\\HI\\HI.M'HI\end{array}\right. & M^{III}\left\{\begin{array}{l}HI\\HI.M'HI\\HI.M'HI\end{array}\right. & M^{III}\left\{\begin{array}{l}HI.M'HI\\HI.M'HI\\HI.M'HI\end{array}\right. & \\
M^{IV}\left\{\begin{array}{l}HI\\HI\\HI\\HI.M'HI\end{array}\right. & M^{IV}\left\{\begin{array}{l}HI\\HI\\HI.M'HI\\HI.M'HI\end{array}\right. & M^{IV}\left\{\begin{array}{l}HI.M'HI\\HI.M'HI\\HI.M'HI\\HI.M'HI\end{array}\right. & \\
M^{V}\left\{\begin{array}{l}HI\\HI\\HI\\HI\\HI.M'HI\end{array}\right. & M^{V}\left\{\begin{array}{l}HI\\HI\\HI\\HI.M'HI\\HI.M'HI\end{array}\right. & M^{V}\left\{\begin{array}{l}HI\\HI.M'HI\\HI.M'HI\\HI.M'HI\\HI.M'HI\end{array}\right. & M^{V}\left\{\begin{array}{l}HI.M'HI\\HI.M'HI\\HI.M'HI\\HI.M'HI\\HI.M'HI\end{array}\right.
\end{array}
$$

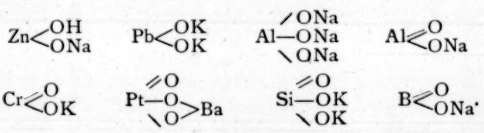
As already shown, representatives of all these classes, except that of the formula $M^{IV}Hl_4.4M^{I}Hl$, are known; and by far the largest number of all the double halides known belong to one or the other of these classes. There are a few which differ from these fundamental forms, but examination shows that they are closely related to these forms. Thus there are compounds of the formulas $2AuCl_3.KCl$, $2AuCl_3.MgCl_2$, $3BiCl_3.2KCl$, etc., but, as will be pointed out further on, the relation between these and the simpler salts is probably similar to that which exists between the salts of the so-called poly-acids and the simpler salts. Certainly the explanation which holds good for the simpler salts is entirely adequate to account for the existence of those of more complex composition.

Finally, there is one exception to the above law known. This is the salt of the composition $CuCl.2KCl$ or $Cu_2Cl_6.4KCl$. While this compound cannot, of course, be ignored, it seems fair, in view of the fact that it is the only exception to the law in nearly four hundred cases, to hope that some explanation will be found for its anomalous composition which will be in harmony with the general law. It should be observed that it is formed from the unsaturated molecule $CuCl$, and this fact may have something to do with the peculiarity of its composition. This point will be referred to again further on.

3. *Analogy between Double Halides and Oxygen Compounds.*

As is well known, many so-called metallic hydroxides, as those of aluminium, chromium, zinc, platinum, and lead, dissolve in the hydroxides of the alkali metals or of the metals of the calcium group, and form salt-like compounds. Several of these have been investigated, and they have been shown to be derived from the more complex hydroxide by the replacement of one or more of the hydrogen atoms by an equivalent number of atoms of the more strongly basic element. Among salts of this kind are the aluminates of sodium and potassium, the chromites, the zincates, the plumbates, etc. The aluminates are, for the most part, derived from the hydroxide $AlO.OH$, which is in turn derived from the normal hydroxide $Al(OH)_3$, by loss of one molecule of water. The chromites are analogous to the aluminates. The zincates are apparently derived from zinc hydroxide by the replacement of one hydrogen atom by an alkali metal. The platinates are derived

from the hydroxide $PtO(OH)_2$, which is in turn derived from the normal hydoxide $Pt(OH)_4$, by loss of one molecule of water. The composition of some of the better known compounds of the kind here referred to is represented by the following formulas:



It requires but a superficial examination to show that, with the exception of the zincate, there is perfect analogy between the composition of these compounds and that of the double halides of the same elements. This is clearly shown by placing the formulas of some of the better known compounds of the two classes side by side thus:

K_2PbO_2	K_2PbI_4
$NaAlO_2$	$NaAlCl_4$
$KCrO_2$	$KCrCl_4$
Na_3AlO_3	K_2CrCl_6
$BaPtO_3$	$BaPtCl_6$
K_2SiO_3	K_2SiF_6
$NaBO_2$	KBF_4
$AlPO_4$	$AlPCl_3$
$FePO_4$	$FePCl_3$

This analogy between the composition of the so-called double halides on the one hand and that of the oxygen compounds on the other is general.

While the oxygen compounds or oxygen salts above referred to are generally formed by the action of a hydroxide upon a hydroxide, for the reason that it is more convenient to work with solutions than with dry substances, it is equally true that the same compounds can be made by bringing together the corresponding oxides, and this mode of formation is strictly analogous to that employed in making some of the double chlorides, as, for example, when dry aluminium chloride is heated with dry potassium chloride. Just as these unite to form the compound $KAlCl_4$, so aluminium oxide and potassium oxide unite to form the compound $KAlO_2$.

As regards the formation of double chlorides in solution, it should be remarked that this mode of formation is not strictly analogous to the formation of oxygen salts by bringing together oxides in solution. In the latter case the water generally acts first upon one or both of the oxides, converting them into hydroxides, and these in turn act upon each other. When a chloride is treated with water, however, there may be decomposition and conversion into the hydroxide either partial or complete. In the latter case the formation of a double chloride cannot take place. For all those cases in which one of the chlorides used is decomposed by water, it is clear that this agent cannot be taken as a solvent. In other cases, and in fact in most cases, in which water is used, this must contain hydrochloric acid to prevent decomposition. In such cases it is probable that the hydrochloric acid unites with one of the chlorides to form a chlor-acid, just as water combines with some of the oxides to form the corresponding hydroxide or oxygen acid. It is well known that many metallic chlorides have the power to unite with hydrochloric acid, and that some of the compounds thus formed are to be regarded as the acids from which the double halides are derived. This is well shown by the compounds H_2PtCl_6 or $PtCl_4.2HCl$, $HAuCl_4$ or $AuCl_3.HCl$, H_2PbI_4 or $PbI_2.2HI$, and H_2HgI_4 or $HgI_2.2HI$.

Finally, the analogy between the double halides and the oxygen compounds of the same elements is shown by the fact that in both cases a compound of either an alkali metal or of one of the members of the calcium group is generally necessary to the formation of the more complex compound. In all cases in which a direct comparison of the formation of double halides with that of the formation of the oxygen salts of the same elements is possible, there is observed perfect analogy as regards the composition of the products.

4. *Acidic and Basic Halides.*

When a metallic hydroxide dissolves in and forms a compound with a strongly basic hydroxide, we speak of the former as having acid properties. Thus aluminium, chromium, and lead hydroxides are said to have acid properties. These properties are not, however, strongly marked, and in order that they may be stimulated to activity, contact with a strongly basic substance is necessary. The substances mentioned do not form salts with

all bases, but only with the strongest ones. But facts of the same order are noticed in connection with the formation of the double halides. Aluminium chloride, for example, does not form double chlorides with all other chlorides, but only with those which are derived from elements with strongly marked basic properties, or with those which are derived from elements with strongly marked acidic properties. Similar facts are observed in the case of other chlorides, so that one is led to the conclusion that just as we have acidic and basic oxides, so too we have acidic and basic halides. In order that oxides may combine to form salts it is necessary in general that one should be acidic and the other basic. And in order further that halides may combine to form double halides, one must be acidic and the other basic, or there must be a certain oppositeness of chemical character which, as far as can be determined, is perfectly analogous to that which we have in mind when we speak of acid and basic properties.

This distinction between acidic and basic halides was first noticed by Von Bonsdorff,[1] and afterwards independently by Boullay.[2] In a letter to M. Gay Lussac, dated December 30, 1826, the former used these words: "En réfléchissant sur la grande analogie qui existe entre l'oxigène et quelques autres corps électro-négatifs par excellence, tels que le chlore, l'iode, etc., surtout par le phénomène du feu ou la combustion, qui a lieu quand ces élémens se combient à d'autres corps simples, et par la propriété que possèdent les mêmes élémens, dans nombre de cas, de gazéifier ces corps, il m'a paru très naturel, au moins très-probable, que les combinaisons de ces élémens avec les autres corps électro-négatifs, de même que les combinaisons de l'oxigène, donneraient naissance à des corps composés analogues aux acides, et que leurs combinaisons avec les corps simples électro-positifs produiraient des corps composés analogues aux bases salifiables."

After describing a number of new double salts he says: "Il se peut bien que je me sois trompé dans ma manière de voir la chose; cependant je hasarde de soumettre mon opinion, quelle qu'elle soit, au jugement des chimistes."

Boullay in the same year referred to this conception in the following words: "Je vais chercher à poser la question nettement et dans toute la simplicité qu'elle paraît avoir reelement. Lorsque l'oxygène se combine avec un autre corps, il en résulte générale-

[1] Ann. chim. phys. **34**, 142 (1826). [2] Ibid. **34**, 337 (1826).

ment un composé doué d'une tendance acide ou basique. L'union de deux composés de ce genre doués de propriétés opposées donne naissance à des sels plus ou moins bien définis. L'idee de sel se rapporte donc toujours à l'union de deux corps composés eux-mêmes.—Sous ce point de vue, les chlorures, les iodures, les sulfures, ne sont point des sels et ressemblant théoriquement aux oxides d'une manière qui paraîtra tout-à-fait évidente à quiconque voudra bien examiner avec attention l'ensemble des travaux qui concernent ces corps. Ce rapprochement admis, les combinaisons de tous ces corps entre eux donnent naissance à diverses séries faciles à caractériser; mais dans l'application, les résultats sont restreints dans des limites souvent étroites par la nature même des corps mis en presence.—En effet, si d'un côté rien ne s'oppose à l'union des oxacides et des oxides, de l'autre aucune réaction particulière ne pourra troubler non plus l'union des sulfures entre eux, des chlorures entre eux, des iodures entre eux, et tous ces composés devront être classés ensemble comme de veritable sels."

Finally, at the close of his paper, Boullay draws this conclusion among others: "Que les iodures métalliques peuvent se partager en iodures acides, et en iodures basiques, et que l'union de ces corps donne naissance à de véritables sels."

Liebig[1] in 1827 commented upon the views of Von Bonsdorff unfavorably, although he says that the opinion of Von Bonsdorff differs but little from that of Berzelius regarding the double fluorides and the sulpho-salts.

Next, Berzelius, in his Jahresbericht[2] for the year 1829, took exception to the views of Von Bonsdorff and of Boullay. His objection is, however, as it appears, mainly one of definition. As sodium chloride is itself a salt, he holds that it cannot also be regarded as a base. The same reasoning would plainly keep us from ascribing acid properties to aluminium hydroxide because it is generally basic. At the time Berzelius wrote, chemists were accustomed to make a sharp distinction between acids and bases and salts, and the idea that one and the same substance could belong to two of these classes at the same time was not entertained. The great influence exerted by Berzelius and by Liebig prevented the general acceptance of the views put forward by Von Bonsdorff and by Boullay, and it seems that the close analogy which exists

[1] Ann. chim. phys. **35**, 68 (1827). [2] Vol. **8**, 138.

between double halides and oxygen salts has since then been almost completely lost sight of. My attention has been called by my friend, Dr. Wolcott Gibbs, to the fact that Dr. Hare of Philadelphia, half a century ago, held the same views as those which were put forward by Von Bonsdorff and Boullay. This is clearly shown by the following extracts from his Compendium, published in 1840: "The *chloro-salts* are generally obtained by mingling chlor-acids with chloro-bases, either in the wet or dry way. In the latter case, heat must be employed in order to facilitate their union. The *bromo-salts* and *iodo-salts* may in general be obtained in the same manner, by mingling brom-acids with bromo-bases, or iod-acids with iodo-bases" (p. 370). In another place (p. 359) he says: "Hence the nine following classes: *oxy-salts*, *sulpho-salts*, *seleni-salts*, *telluri-salts*, *chloro-salts*, *bromo-salts*, *iodo-salts*, *fluo-salts*, and *cyano-salts*. Obviously, of these the first four are formed by the *amphigen bodies*, and the rest by the *halogen bodies* of Berzelius."

Further, in a paper published in Philadelphia in 1842, entitled "An Effort to refute the Arguments advanced in favor of the Existence in the Amphide Salts, of Radicals, consisting, like Cyanogen, of more than one Element," Dr. Hare discussed at some length the relations existing between the oxy-salts and the double halides.

It appears that Kane, Graham, and others took the ground with Berzelius that the halogen salts could not be regarded as acids and bases because they are salts. Dr. Hare saw clearly that the question was one of definition. He offered the following definition of salts, which he conceived "to be justified by the practice of modern chemists in general": "When two compounds, capable of combining with each other to form a tertium quid, have an ingredient common to both, and one of the compounds prefers the positive, the other the negative pole of the voltaic series, we must deem the former an acid, the latter a base."

At the present time there is no difficulty in recognising the close analogy between the halides and the oxides and sulphides. If we speak of sodium chloride as a salt, we do not hold that it is in any way fundamentally different from sodium oxide or sodium sulphide. Everything depends upon our definitions of acids and salts, and these definitions are unquestionably far from satisfactory. If we call sodium chloride a salt because it is derived from hydrochloric acid by the replacement of the hydrogen by sodium, we

may with equal right call sodium hydroxide and sodium oxide salts, because they are derived from water by replacing part or all the hydrogen of the water by sodium. There is a difference in the ease with which the replacement can be accomplished in the two cases, but probably no one will maintain that the two acts differ fundamentally. Whatever we may call the compounds, then, it appears from a consideration of the facts discussed in the first part of this paper, that the action of halides upon halides is analogous to the action of oxides upon oxides, and that the compounds formed in the two cases are also analogous, not only in composition, but in their nature and structure. Whatever the power may be which makes it possible for two oxides of opposite chemical properties to act upon each other and form a neutral compound, it appears that this same power exists in halides.

The analogy between the formation of oxygen salts and double halides would appear more striking if we should regard the salts as formed by the action of an acidic oxide upon a basic oxide, or, in other words, if we should go back to the conception of this act which prevailed before the introduction of the so-called unitary system. That old conception is still as true as it ever was. The oxides can be divided into two classes with reference to their conduct towards one another. When an acidic oxide as, for example, sulphur trioxide, acts upon a basic oxide, as, for example, potassium oxide, a salt is formed according to the equation:

$$SO_3 + K_2O = K_2SO_4.$$

When, however, this same acidic oxide acts upon water, a substance which we call an acid is formed:

$$SO_3 + H_2O = H_2SO_4.$$

The two acts are of the same character, as is generally recognised. The formation of the acid or of the hydrogen salt is the first stage in the process of the formation of the salt. The formation of the other salts is effected by the replacement of the hydrogen of the so-called acid. The fundamental act in the formation of salts is, however, not this act of substitution, but the union of the water, which in this case acts as a basic oxide towards the acidic oxide. Going back then to this view in regard to the formation of oxygen salts, the analogy between this act and that of the formation of double chlorides will be clearly recognised.

But further, just as acidic oxides combine with water to form

hydrogen salts or acids, so also some halides combine with halogen acids to form hydrogen salts or acids, which differ from the oxygen acids in containing a halogen in place of oxygen. The two acts are in all probability perfectly analogous, though the latter is much less common than the former. The following cases will suffice to illustrate this analogy:

$$SO_3 + H_2O = H_2SO_4$$
$$CO_2 + H_2O = H_2CO_3$$
$$PtCl_4 + 2HCl = H_2PtCl_6$$
$$SiF_4 + 2HF = H_2SiF_6$$
$$AuCl_3 + HCl = HAuCl_4$$
$$Cl_2O_3 + H_2O = 2HClO_2$$
$$B_2O_3 + H_2O = 2HBO_2.$$

Although the number of compounds of the kind here referred to thus far prepared is small, it is of importance to notice that in composition they are perfectly analogous to the so-called double salts formed by the combination of metallic chlorides, just as the oxygen acids formed by combination of water with acidic oxides are generally analogous in composition to the oxygen salts.

It appears from the above considerations that the halogen acids, or, to take one case, that hydrochloric acid, bears to double chlorides much the same relation that water bears to oxygen salts. We can easily conceive of a *chlorine system of chemistry* analogous to the *oxygen system*, which, owing to natural conditions, we are necessarily more familiar with. It is probable that, if we could use the compound hydrochloric acid as a solvent as we use the corresponding oxygen compound, water, we should be much more familiar with double chlorides than we now are. In our present system oxygen is the controlling element, and water is the most common reagent. Most double halides are decomposed by water, and, as we are generally forced to use water in making these compounds, it is clear that we start with unfavorable conditions for dealing with these salts. In the oxygen system water is the connecting link between acids and bases. We speak of it as neutral. Why? Because it does not act upon those compounds which we call acids, nor upon those which we call bases. Towards acidic oxides, however, it is unquestionably basic, and towards basic oxides like potassium, sodium and calcium oxides, it is unquestionably acid. In the chlorine system, hydro-

chloric acid bears a similar relation to the acidic chlorides on the one hand, and also towards the basic chlorides on the other. It is the connecting link between the acidic and the basic chlorides. These remarks apply with equal force to the other halogens.

A case of the same kind is presented by sulphur. As is well known, sulphides combine with one another in much the same way that oxides do, and form the sulpho-salts, which in composition are again perfectly analogous to the oxygen salts. Not many of these are known, but quite enough to show the analogy to the oxygen salts. The principal reason why not more are known appears to be, as in the case of the double halides, the fact that most of them cannot exist in the presence of water. In the sulphur system, hydrogen sulphide occupies the same position that water does in the oxygen system, and in order to work to the same advantage with the sulpho-salts we should have hydrogen sulphide available as a solvent. Probably no thinking chemist doubts that there is complete analogy between the sulpho-salts and the oxygen salts, and yet the evidence in favor of this view is, I think, by no means as strong as that upon which the view that the double halides are analogous to oxygen salts is founded.

4. *Theoretical.*

Thus far I have carefully abstained from putting forward any theory regarding the constitution of the double halides. But, if it is acknowledged that the evidence furnished by the facts is sufficient to show that the act involved in the formation of the double halides is of the same kind as that involved in the formation of oxygen salts, and that the products in the two cases are of the same general character, then the only explanation which suggests itself is this:

Two halogen atoms acting together can play the same part that the so-called linking oxygen atom plays in oxygen salts.

This view was first expressed by Naquet in his Principes de Chimie,[1] which appeared in 1867. On page 62 he gives this formula $\frac{Ag}{K}>Cl_2^{II}$ to the compound formed by the union of potassium chloride and silver chloride. His explanation of the compound $HgI_2.2KI$, given on page 61, is much less satisfactory. In the same year Dr. Wolcott Gibbs[2] suggested that in the double

[1] Principes de Chimie fondée sur les Théories Modernes. Par A. Naquet. Paris, 1867.

[2] American Journal of Science (2 Series) **44**, 409 (1867).

halides perhaps two halogen atoms might play the part of one oxygen atom, and gave, by way of illustration, these formulas to acid potassium fluoride and potassium hydroxide:

$$\left.\begin{matrix} K^{III}F_2 \\ H \end{matrix}\right\} \text{or } K^{III}(HF_2),$$

$$\text{and} \quad \left.\begin{matrix} K^{III}O^{II} \\ H \end{matrix}\right\} \text{or } K^{III}(HO).$$

It will be seen that at that time Dr. Gibbs held that potassium might act as a trivalent element, and he conceived the union between the hydrogen and the fluorine, and between the hydrogen and the oxygen, to be effected through this polyvalent potassium.

The fullest and clearest statement concerning the structure of the double halides is that of Blomstrand, published in his Chemie der Jetztzeit[1] in 1869. In my opinion, this book is not as much read as it deserves to be. There are many original views put forward in it, and chemical phenomena are throughout treated in a broad way, indicating clear insight. The discussion regarding the halogen double salts is well worthy of careful study. The author expresses himself concerning these compounds thus (p. 340):

"Die Haloiddoppelsalze entsprechen vollständig den eigentlichen Amphidsalzen, oder die in Doppelatomen wirkenden Haloide spielen durchaus dieselbe chemische Rolle, wie die wahren Amphide."

He conceives the halogen atoms to be trivalent, and explains the linking by formulas like the following:

$$Mg\!<\!\begin{matrix} Cl \\ Cl{=}ClK \end{matrix} \quad \text{and} \quad Pt\left\{\begin{matrix} Cl \\ Cl{=}ClK \\ Cl{=}ClK \\ Cl \end{matrix}\right.$$

The formulas given by Blomstrand differ somewhat in appearance from these, but they are evidently intended to express essentially the same conception.

In 1877 Jörgensen[2] made use of the same conception to explain chloroplatinic acid, which he expressed by the formula $Cl_2Pt\!<\!\begin{matrix} Cl_2H \\ Cl_2H \end{matrix}$.

In 1881 Professor Mallet[3] advanced the same explanation for the

[1] Die Chemie der Jetztzeit vom Standpunkte der electrochemischen Auffassung aus Berzelius Lehre entwickelt. Von C. W. Blomstrand, Professor an der Universität zu Lund. Heidelberg, 1869.

[2] J. prakt. Chem. **16**, 352.

[3] This Journal **3**, 189 (1881).

double fluorides, after he had shown that at 30° the specific gravity of hydrofluoric acid gas corresponds to the formula H_2F_2. In his Kurzes Lehrbuch der Anorganischen Chemie, Kolbe suggests that possibly the double chlorides may be explained in the above way; and quite recently Francke,[1] in order to explain certain compounds of manganese obtained by him, has adopted the view that a double chlorine atom may take the place of an oxygen atom. In his Chemical Philosophy, Professor Cooke[2] suggests (p. 515) the possibility of such a double chlorine atom, not as an explanation of the double chlorides, but to account for the fact that crystallised stannic chloride, $SnCl_4.5H_2O$, retains two molecules of its water when heated. He thinks it possible that the salt which is left may have the formula

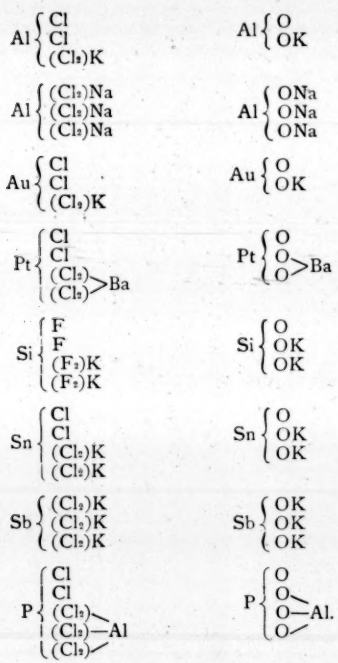
$$Sn\begin{cases} OH \\ OH \\ Cl_2H \\ Cl_2H \end{cases}.$$

Professor Cooke evidently considers some of the double salts as molecular compounds, while he speaks of potassium chloroplatinate as a salt of the acid of the formula $H_2PtCl_6.6H_2O$, without giving an explanation of this formula.

In 1885 Armstrong[3] put forward the view that the double chlorides might be compounds of molecules held together by surplus affinity, and he gives the formula $Hg\overset{Cl.ClK}{Cl.ClK}$ to the double chloride of mercury and potassium. Finally Heyes,[4] in discussing the subject of valency and validity, also suggested that the double halogen salts may be explained by assuming that the halogen atoms combine with each other.

From the above it is evident that the idea that two chlorine atoms can take the place of one oxygen atom in salts is not a new one, though it has certainly not been generally accepted. In accordance with this view, the constitution of some of the more common double halides may be represented by the following formulas, by the aid of which the analogy between these compounds and the oxygen compounds is clearly seen:

[1] Francke, J. prakt. Chem. [N. F.], **36**, 451 (1887).
[2] Principles of Chemical Philosophy. By Josiah Parsons Cooke. Boston, 1881.
[3] British Assoc. Reports, 1885, 959.
[4] Philosophical Magazine **25**, 221, 297.


Al Cl Cl (Cl2)K
Al O OK
Al (Cl2)Na (Cl2)Na (Cl2)Na
Al ONa ONa ONa
Au Cl Cl (Cl2)K
Au O OK
Pt Cl Cl (Cl2) (Cl2) >Ba
Pt O O O >Ba
Si F F (F2)K (F2)K
Si O OK OK
Sn Cl Cl (Cl2)K (Cl2)K
Sn O OK OK
Sb (Cl2)K (Cl2)K (Cl2)K
Sb OK OK OK
P Cl Cl (Cl2) (Cl2) —Al (Cl2)
P O O O—Al. O

As will be seen, all that is required is that we assume the power of a halogen atom to unite with itself to form a bivalent group, and we have a satisfactory theory to account for the large class of compounds with which we are dealing. As I have already said, there are some compounds included in the class which do not correspond in composition to any one of the fundamental forms. These can, however, be easily explained, just as we explain the salts of the poly-acids. Thus we have not only the cases given on p. 298, viz:

$2AuCl_3.KCl$ or KAu_2Cl_7
$2AuCl_3.MgCl_2$ or $MgAu_2Cl_8$
$3BiCl_3.2KCl$ or $K_2Bi_3Cl_{11}$,

but more complex ones, of which those represented by the following formulas are fair examples:

$2ZnI_2.KI$ or KZn_2I_5
$2ZnI_2.BaI_2$ or $BaZn_2I_6$
$2HgCl_2.RbCl$ or $RbHg_2Cl_5$
$4TaF_5.3KF$ or $K_3Ta_4F_{11}$
$2SbI_3.3KI$ or $K_3Sb_2I_9$
$2SbI_3.3NaI$ or $Na_3Sb_2I_9$
$3AlF_3.5NaF$ or $Na_5Al_3F_{14}$
$2ClF_4.3KF$ or $K_3Cl_2F_{11}$.

The salt KAu_2Cl_7 is evidently derived from an acid HAu_2Cl_7. The more common form of chlorauric acid is $HAuCl_4$. The relation between the two is expressed by the equation:

$$2HAuCl_4 = HAu_2Cl_7 + HCl;$$

or perhaps better by the formulas:

$$Au\begin{cases} Cl \\ Cl \\ (Cl_2)H \end{cases} \qquad Au\begin{cases} Cl \\ Cl \\ (Cl_2) \end{cases} \quad Au\begin{cases} Cl \\ (Cl_2)H \end{cases}$$

The salt $MgAu_2Cl_8$ is derived from the acid $H_2Au_2Cl_8$. This is related to the fundamental acid, as shown thus:

$$Au\begin{cases} Cl \\ Cl \\ (Cl_2)H \end{cases} \qquad Au\begin{cases} (Cl_2)H \\ Cl \\ (Cl_2) \end{cases} \quad Au\begin{cases} Cl \\ Cl \\ (Cl_2) \end{cases} \text{ or } \quad Au\begin{cases} Cl \\ (Cl_2)H \end{cases} \quad Au\begin{cases} (Cl_2)H \\ (Cl_2)H \end{cases}.$$

The salt $K_2Bi_2Cl_{11}$ is derived from the acid $H_2Bi_2Cl_{11}$, and this is related to the fundamental form H_3BiCl_6 as shown below:

$$3H_3BiCl_6 = H_2Bi_2Cl_{11} + 7HCl;$$

$$Bi\begin{cases} (Cl_2)H \\ (Cl_2)H \\ (Cl_2)H \end{cases} \qquad Bi\begin{cases} (Cl_2)H \\ Cl \\ (Cl_2) \end{cases} \quad Bi\begin{cases} Cl \\ (Cl_2) \\ (Cl_2) \end{cases} \quad Bi\begin{cases} Cl \\ (Cl_2)H \end{cases}$$

One more example will suffice. The salt $BaZn_2I_6$ is derived

from the acid $H_2Zn_2I_6$, and this is related to the fundamental form H_2ZnI_4 as shown below:

$$2H_2ZnI_4 = H_2Zn_2I_6 + 2HI;$$

$$Zn\begin{cases}(I_2)H\\(I_2)H\end{cases} \qquad Zn\begin{cases}(I_2)H\\I_2\\Zn\end{cases}\begin{cases}(I_2)H\end{cases}$$

The analogy between these relations and those which exist between the corresponding oxygen compounds will appear without explanation, though one case may be given. For the purpose of direct comparison the last case cited serves very well. We can easily conceive of the existence of a hydroxide of zinc of the formula $H_2Zn_2O_3$ derived from the normal hydroxide $Zn(OH)_2$. These relations are expressed thus:

$$Zn\begin{cases}OH\\OH\end{cases} \qquad Zn\begin{cases}OH\\O\\Zn\end{cases}\begin{cases}OH\end{cases}$$

Plainly this compound $H_2Zn_2O_3$ is analogous to the iodine compound $H_2Zn_2I_6$. All the other complicated cases can be explained as readily as those cited.

In the mixed double halides it is necessary to assume that two halogen atoms of different kinds acting together play the part of the double chlorine atom in the double chlorides, and of the oxygen atom in the oxygen salts. The structure of the compound formed by the union of antimony trichloride and potassium bromide, for example, should be represented thus:

$$Sb\begin{cases}(ClBr)K\\(ClBr)K\\(ClBr)K\end{cases} \quad \text{or} \quad Sb\begin{cases}(BrCl)K\\(BrCl)K\\(BrCl)K\end{cases}$$

It is probable that the linking group would adjust itself in accordance with the affinities, and if, as is assumed in the valence hypothesis, a definite arrangement of the atoms with reference to one another exists in the molecule, the more probable view is that the structure should be represented by the following formula:

$$\begin{array}{l} \diagup Br-ClK \\ Sb-Br-ClK, \\ \diagdown Br-ClK \end{array}$$

for the reason that the specific affinity of chlorine for potassium is greater than that of bromine for antimony. This would explain

why it is that the same salt is formed by union of antimony trichloride and potassium bromide that is formed by union of antimony tribromide and potassium chloride, a fact which was brought to light by R. W. Atkinson[1] working in Williamson's laboratory. The explanation is not a forced one, for, as is well known, the halogens exchange places with the greatest ease when their metallic salts are brought together.

With regard to the salt which differs in its composition from all the other double halides, viz. that of the formula $CuCl_2.2KCl$, attention has already been called to the fact that it is derived from the unsaturated compound CuCl. Whether this has anything to do with its anomalous composition can only be determined by further investigation, and work bearing upon this point has already been begun in this laboratory. Blomstrand does not hesitate to assume that a triple chlorine atom can play a part somewhat like that played by the double chlorine atom, and according to this he represents the compound of cuprous chloride and potassium chloride by this formula: $Cu''<^{Cl.Cl.ClK_2}_{Cl.Cl.ClK_2}$.

In terms of the valence hypothesis this view is expressed thus:

$$Cu - Cl = Cl - Cl<^{K}_{K}.$$

Whatever the correct explanation of this compound may be, it is clear from the facts that the condition existing in it is an unusual one. The above formula appears to me to be highly speculative, and before offering any other or making any further effort to explain the compound, it seems to me better to wait until we have more facts at disposal. Before leaving this part of the subject, however, I will again call attention to the fact that this is the only well-authenticated exception to the simple conception of double halides in a list of nearly four hundred compounds.

The question as to whether the chlorine in these compounds is to be regarded as bivalent or trivalent is one which will be asked. Blomstrand, as we have seen, regards it as trivalent. I cannot see that at present we have any evidence which justifies us in the use of the expression $-Cl=Cl-$ rather than $-Cl-Cl-$. It is possible that as investigation proceeds, light may be thrown upon this part of the subject. Perhaps the study of such compounds as that of the formula $CuCl_2.2KCl$ may be of service in this

[1] J. Chem. Soc. **43**, 289 (1883).

direction. At present all that we can fairly say is that *the double halogen atom acts like the linking oxygen atom, and is therefore bivalent.*

5. *Objections to the Theory.*

What objection can be offered to the theory of double halides discussed in the preceding pages? The one which undoubtedly has, and perhaps will have, the most weight with the great majority of chemists is that it is not in accordance with the prevailing views regarding the valence of the halogens. Horstmann in his Theoretische Chemie[1] (p. 340) says in regard to this subject: "Die Halogendoppelsalze sind fast so zahlreich als die Sauerstoffsalze und haben mit denselben sehr häufig unverkennbare Analogien, die man früher mehr beachtete als heute." After giving some examples, he says further: "Berücksichtigt man, dass der chemische Charakter mancher Elemente den Halogenen gegenüber sich wohl etwas anders äussern kann, als dem Sauerstoff gegenüber, so erkennt man in dem vorstehenden Beispiele den vollkommenen Parallelismus mit den Sauerstoffsalzen, welche die zeitweilig übliche Bezeichnung jener Doppelverbindungen als Chlorosalze (Bromosalze, etc.) rechtfertigt. Als weitere Abtheilung der Salze würden noch die Schwefeldoppelverbindungen oder Sulfosalze hinzukommen.—Nach dualistischer Ansicht, mit Benutzung der alten Aequivalentgewichte, konnte allen diesen Verbindungen analoge Constitution zuerkannt werden. Aber die Valenzlehre hat die Analogie gestört. Nur die Verbindungen des zweiwerthigen Sauerstoffs und Schwefels konnten durch Atomverkettung erklärt werden. Die Chlorosalze und die entsprechenden Salze der anderen Halogenen blieben als dualistisch zusammengesetzte Molecularverbindungen zurück.—Nun würde der atomistische Zusammenhalt aller solchen Halogenverbindungen erklärlich sein, wenn man sich darin die Halogene mehrwerthig wirkend vorstellen dürfte. Allein die früher angeführten Gründe sprechen für die Mehrwerthigkeit der Halogene nur in ihren Verbindungen mit dem negativen Sauerstoff, nicht mit den positiven Metallen. Jene Erklärung ist daher nicht sehr wahrscheinlich. Sie könnte höchstens für einige Doppelverbindungen des Fluors, z. B.

[1] Lehrbuch der Physikalischen und Theoretischen Chemie. Von A. Horstmann und H. Landolt. Zweite Abtheilung. Theoretische Chemie einschliesslich der Thermochemie. Von A. Horstmann. Braunschweig, 1885. (This is a part of the first volume of the last edition of Graham-Otto's Ausführliches Lehrbuch der Chemie.)

$HNaF_2$, gerechtfertigt scheinen, weil die Dampfdichte der Fluorwasserstoffsäure selbst bei niedriger Temperatur auf die Molecularformel H_2F_2 und auf die Zweiwerthigkeit des Fluors hinweist."

Horstmann then goes on to say that another explanation is on the whole more desirable, or at least that it appears to be capable of wider application (scheint allgemeiner anwendbar zu sein). The other explanation is this, that the formation of double halides is due to the stimulating effect of the alkali salt of the halogen upon the other halide. Just as we commonly explain the union of ammonia with hydrochloric acid by assuming that under the influence of the hydrogen and chlorine the nitrogen of the ammonia becomes quinquivalent, so he thinks it probable that, when potassium chloride acts upon platinic chloride, the platinum becomes octovalent. Such compounds as $SbCl_3.KBr$, $SbCl_3.2KCl$, and $SbCl_3.3KCl$, would, according to this, necessitate the assumption that antimony can act with a valence of five, of seven, and of nine! Similar results are reached in an attempt to apply this hypothesis to the compounds of aluminium and of chromium. Horstmann's objection to the view that the halogens may be polyvalent in the double halides is that the study of other compounds leads to the conclusion that the halogens exhibit polyvalence only towards oxygen. So also it might with equal force be objected to the explanation which he accepts, that the study of other compounds of antimony and of aluminium does not justify the assumption that they can act with a valence of nine. The question is, *what conclusion does the study of the double halides themselves lead to?* I hold that this study leads unmistakably to the conclusion that in them the halogen atoms, or some of these atoms, are polyvalent. We do not now hesitate to accept the conclusion that the halogens are polyvalent towards oxygen, whereas a few years ago this idea met with but little favor. We cannot further, as it seems to me, avoid the conclusion that the halogens are polyvalent towards one another. How else can we rationally explain the compounds ICl_3 and IF_5? But, if the halogens can combine directly with each other and form comparatively stable compounds, it is not surprising that when they are in combination with metallic elements the compounds which they form should be more stable. It appears to me, however, that the strongest argument in favor of the polyvalence of the halogen atoms in the double halides is to

be found in the unmistakable analogy between these compounds and the oxygen salts which was discussed so fully in the early part of this paper. Horstmann clearly recognises this analogy. He speaks of the perfect parallelism which exists between the two classes of compounds. When it comes to the explanation he is willing to lose sight of this analogy and take refuge in an hypothesis which can fairly be said to be much less probable than the one which he discards. The analogy between the double halides and the oxygen salts is perfectly clear to him, yet he says, "Aber die Valenzlehre hat die Analogie gestört." I should rather say that the valence hypothesis in its old rigid form has prevented chemists from recognising the analogy, and has prevented them from using analogous expressions for analogous compounds; and I cannot help feeling that, on a reconsideration of the facts, so fair-minded a man and so clear a thinker as Professor Horstmann will agree with me on this point. To which should we give the greater weight, to one phase of the imperfectly developed and ever-changing valence hypothesis, or to a large number of well established facts? Can any one be in doubt?

I have given special attention to the views of Horstmann because they are put forward by a man of recognised pre-eminence and in a book which deservedly has great influence; and, further, because I believe that his presentation of the case is as strong as it can be made from the point of view of those who are under the subjection of the valence hypothesis. I suppose that the majority of chemists think as Professor Horstmann does, or at least they accept the same conclusion without thinking. I have been surprised to find that that cautious writer and philosopher, Professor Lothar Meyer, is not willing to adopt the view that the halogens are polyvalent in the double halides, but that he is inclined to accept an explanation like that accepted by Horstmann. He remarks on this subject: "Der Annahme aller dieser Formeln steht aber das eine schwere Bedenken gegenüber, dass man in ihnen Fluor und Chlor auch dem positiven Wasserstoffe und den Metallen gegenüber mehrwerthig annehmen muss, wozu sonst keine Nöthigung vorliegt."[1] To this argument the same reply is justified as that already made to the similar argument of Horstmann. The question is, what conclusion does the study of the double halides themselves lead to?

[1] Die Modernen Theorien der Chemie und ihre Bedeutung für die chemische Mechanik von Dr. Lothar Meyer, 5te Auflage, 1884.

6. *Applications.*

If it be true that chlorides can combine with other chlorides through the chlorine atoms, as I think has been shown, it is quite possible that this linking power of halogens may make itself felt in other similar cases. Thus it seems to me probable that aluminium chloride, instead of existing under ordinary circumstances as the simple molecule $AlCl_3$, is itself a compound analogous to the double halides, having the formula $Al\begin{smallmatrix}/(Cl_2)\backslash\\-(Cl_2)-\\\backslash(Cl_2)/\end{smallmatrix}Al$.[1] If this is the constitution of aluminium chloride, we can quite understand why such peculiar results should be obtained in the determination of the specific gravity of this compound. These results show clearly that at temperatures just above the boiling point, the specific gravity is in accordance with a more complex formula. It is probable that the molecules at the lower temperature have the formula Al_2Cl_6, and that when the temperature is raised these break down gradually to the simpler form $AlCl_3$. The formation of an ordinary double chloride from aluminium chloride is not, according to this view, a simple addition, but it involves a preliminary breaking down, as represented in this equation:

$$Al_2Cl_6 + 2KCl = 2KAlCl_4.$$

The above view, further, would explain why the compounds of aluminium with organic radicals correspond to the simpler formulas, as, for example, $Al(CH_3)_3$, $Al(C_2H_5)_3$, as shown to be the case by the recent work of Quincke.[2] Of course, if the above arguments are of value with reference to the case of aluminium chloride, a similar explanation appears probable in the case of other metallic chlorides.

Another thought suggests itself. No satisfactory explanation has yet been offered for the reaction of Friedel and Crafts for the synthesis of hydrocarbons. It is, however, generally conceded that the aluminium chloride used in the reaction forms an unstable compound with the halogen derivative. The formation of such compounds is easily understood if we concede to chlorine the linking power. Just as aluminium chloride and potassium chloride combine to form the stable potassium chloraluminate, so we can

[1] See also Heyes, Philosophical Magazine **25**, 307.

[2] Ber. d. chem. Gesell. **22**, 551 (1889).

easily conceive that ethyl chloride and aluminium chloride may combine to form the unstable compound, ethyl chloraluminate, $C_2H_5AlCl_4$. In this compound, further, a part of the chlorine would probably be held much less firmly, and be better able to enter into reaction than the chlorine of either ethyl chloride or of aluminium chloride taken separately. Or it may be that in some cases a compound of the halogen derivative with aluminium chloride is not formed, but that the disturbing influence of the aluminium chloride is felt in its attraction for the chlorine of the halogen derivative, so that the latter is less stable and more susceptible to reagents than when the aluminium chloride is not present. Granted the linking power of chlorine, and the action of aluminium chloride in the Friedel and Crafts reaction is, it appears to me, no longer mysterious.

7. *Nomenclature.*

The acceptance of the views above set forth concerning the nature and constitution of the double halides will necessarily lead to a revision of the nomenclature of these compounds in harmony with that proposed by Von Bonsdorff, Boullay, and Hare. In some cases chemists have adopted the better names without at the same time adopting the conception of the compounds upon which the names are founded. Thus it has become more and more customary to speak of fluosilicates and of chloroplatinates, but in most cases the older names, such as double chloride of magnesium and potassium, double chloride of chromium and sodium, are still used. The change required by the acceptance of the view that the double chlorides are chloro-salts is simple and will suggest itself. Just as the salts formed with platinic chloride are called *chloroplatinates*, so those with aluminic chloride should be called *chloraluminates;* those with magnesium chloride, *chloromagnesates;* those with zinc chloride, *chlorozincates;* those with auric chloride, *chloraurates*, etc., etc. So, also, the acids from which these salts are derived should be named as *chloroplatinic* acid is named. We should speak of *chlorauric acid*, of *iodoplumbous acid*, of *iodohydrargyric acid*, etc., etc. That some of these names lack elegance can scarcely be urged as a serious objection to their use. It may safely be said that they are more elegant, as in every other respect more satisfactory, than those at present in use.

8. *Summary and Conclusion.*

In the foregoing I have called attention:

(1) To the large number of the substances known as double halides.

(2) To the simplicity of the law governing the composition of these compounds.

(3) To the analogy of these compounds with the oxy-salts.

(4) To the arguments which lead to the conclusion that there are in general two classes of halides, which we may regard as basic and acidic, and which bear to each other the same relations that basic oxides bear to acidic oxides.

(5) To the arguments which, as it appears to me, fully justify the conclusion that in the double halides we have a double halogen atom playing the same rôle that the linking oxygen plays in oxy-salts.

Further, let me again say that the views expressed in this paper have in past years, in one form or another and in a more or less comprehensive way, been advocated by others. My object is to direct the attention of chemists to the character of the evidence which is available, as I believe that an unprejudiced study of this evidence will lead to the acceptance of the views put forward, and I feel sure that this will contribute to a more rational treatment of a large class of chemical compounds, and to a clearer conception of a large class of chemical phenomena.

I propose in the future to devote a part of my time to experimental work bearing upon the double halides, and two investigations in this field have already been begun in this laboratory. Some of the work done in former years evidently needs revision, and at first attention will be directed chiefly to such revision. There are, however, several lines which may, I think, be followed with profit, though, as we have already found, the work involves serious experimental difficulties.

As regards the work thus far begun, I may say that Mr. G. M. Richardson is at present investigating some of the compounds obtained from stannous chloride, with the main object of determining whether this unsaturated compound is capable of yielding other chloro-salts besides those of the general formula M_2SnF_4; and Mr. C. H. Herty has been engaged for some time in the study

of the iodoplumbates, which were first studied by Boullay in 1826.[1] Some interesting results have been obtained in the course of this investigation. In anticipation of the publication of the complete results, it may be stated now with confidence that a salt of the composition $PbI_2.4KI$ or K_4PbI_6, as described by Boullay, cannot be made by the method described in his paper; and that the one salt formed with most ease when lead iodide and potassium iodide are brought together under a great variety of circumstances, has the composition $KPbI_3 + H_2O$ or $PbI_2.KI + H_2O$. The chloroplumbates and bromoplumbates as well as the mixed double halides of lead, if they can be obtained, will also be made the subject of study. Many other subjects for work in this field suggest themselves, and it is hoped that some of these at least can be taken up in the immediate future.

JOHNS HOPKINS UNIVERSITY, CHEMICAL LABORATORY, *May*, 1889.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

III.—ON THE CONDUCT TOWARDS ALCOHOL OF THE DIAZO COMPOUNDS OBTAINED FROM THE THREE NITRANILINES, AND OF THOSE OBTAINED FROM THE THREE AMIDO-BENZOIC ACIDS.

BY IRA REMSEN AND R. O. GRAHAM.

In an earlier investigation,[2] Orndorff and one of us have shown that when the salts of diazo-benzene are decomposed in alcohol, phenetol is the main product, but little benzene being formed; and, further, that the salts of ortho- and meta-diazo-toluene conduct themselves differently from those of the isomeric para-compound. About 50 per cent. of ortho-diazo-toluene sulphate is converted by alcohol into the ethyl ether of ortho-cresol; and about 40 per cent. of the meta-compound undergoes the same transformation; while, when para-diazo-toluene sulphate is decomposed in alcohol, about 45 per cent. is converted into toluene, and 18 per cent. into the ethyl ether of para-cresol. As it was thus shown that the presence of the methyl group exerts an influence on the course of

[1] Ann. chim. phys. [2 Série] **34** (1827).

[2] See this Journal **9**, 387.

the reaction, it became desirable to investigate other cases, in order, if possible, to discover whether other groups also exert an influence, and whether this is the same as that exerted by methyl. The first case examined was that of the three diazo-compounds obtained from the nitranilines. Then we took up the three diazo-compounds formed from the amido-benzoic acids.

Experiments with the Nitro-diazo-benzenes.

Preparation of ortho-nitraniline.—Ortho-nitraniline was prepared according to the method described by Körner,[1] by treating acetanilide with nitric acid of specific gravity 1.465. Körner advises that the acid employed be free from the lower oxides of nitrogen. But an acid of the above specific gravity, which was prepared by mixing ordinary concentrated and fuming nitric acids, was found to be more satisfactory than the acid when free of the lower oxides. The treatment with nitric acid was conducted as described below. Several small beakers were placed in shallow pans filled with powdered ice. Into each of these, twenty grams of the acid were poured, and then 10 grams powdered acetanilide thrown upon the acid. After a few moments, a violent reaction took place; and when this was over, the contents of the beaker were thrown into a large evaporating dish containing lumps of ice. After all the acetanilide had been converted into the nitro-compound, the latter was filtered from the ice-water, and then thrown into an excess of a strong solution of potassium hydroxide. A mixture of para- and ortho-nitranilines was thus obtained. By distilling in steam for several days, the volatile ortho-nitraniline was carried over with the water-vapor. About 1200 grams of acetanilide yielded 115 grams of ortho-nitraniline. By heating the non-volatile portion with very dilute alcohol, filtering, and boiling with bone-black, the para-nitraniline was obtained pure.

Preparation of ortho-diazo-benzene nitrate.—This salt was prepared as follows: 10 grams ortho-nitraniline were treated in a flask with 45 cc. dilute and a little concentrated nitric acid. The flask containing the solution of the nitrate thus formed was placed in ice-water, and a rapid current of nitrogen trioxide passed through the liquid, until completion of the reaction was indicated by the free escape of nitrogen trioxide. The contents of the flask were filtered

[1] Jahresbericht für Chemie, 1875, 344.

and the filtrate placed in a freezing mixture. The thoroughly cooled liquid was treated with 200 cc. cold anhydrous ether, the two being thoroughly shaken together. Then 75 cc. cold alcohol were added, and the mixture thoroughly shaken in the freezing mixture. Under these circumstances the diazo-compound crystallised out. It was quickly filtered, washed with ether, and then spread upon filtering paper. 10 grams ortho-nitraniline yielded 9 grams ortho-nitro-diazo-benzene nitrate. In one attempt to precipitate the diazo-compound by placing the liquid containing it in a freezing mixture and adding alcohol, an active decomposition began at once, and this ended in a violent explosion.

Ortho-nitro-diazo-benzene nitrate forms small tabular crystals which at first are pure white, but they change almost immediately to golden yellow. The compound explodes when heated, but not by concussion. It is easily soluble in water.

Ortho-nitro-diazo-benzene sulphate was made in the same way as the nitrate. 10 grams ortho-nitraniline yielded 11 grams of the sulphate. The salt, which is colorless and very stable, crystallises in small plates. It is not decomposed by concussion; and when heated it explodes feebly. If a free flame is brought in contact with it, it puffs up and becomes charred.

Decomposition of ortho-nitro-diazo-benzene sulphate by alcohol.—The dried salt was brought into a dry flask with absolute alcohol, and, after the flask was connected with an inverted condenser, gently heated on the water-bath. Decomposition began when the temperature of the water-bath reached 70°, and it then proceeded quietly to the end. A strong odor of aldehyde was noticed. The reaction was a very clean one. On distilling in steam, nitrobenzene passed over, and in the flask a small quantity of a brown semi-crystalline solid remained, but this could not be purified by crystallisation. 22 grams of the sulphate yielded 9 grams nitrobenzene, a yield which amounts to 54 per cent. of the theoretical.

Attempts were made to obtain the products of the decomposition of the sulphate by water and in toluene, but in the former case only a tar was formed, and from this no definite product could be isolated; while on heating with toluene, even at the boiling point of the hydrocarbon, no action took place for some time, when suddenly the entire quantity decomposed at once, causing vigorous explosion, but only a tarry mass was left behind.

Preparation of meta-nitro-diazo-benzene nitrate.—10 grams

meta-nitraniline were thoroughly mixed with 15 cc. strong, and a little dilute, nitric acid, and the nitrate thus formed. This was suspended in 100 cc. absolute alcohol in a flask surrounded by ice-water, and a rapid current of the oxides of nitrogen passed through the liquid for an hour. The diazo-compound was precipitated out as fast as it was formed. At the end of the operation a little ether was added, and the liquid placed in a freezing mixture for the purpose of completing the precipitation of the diazo-compound. The compound was filtered with the aid of the pump, washed with absolute alcohol and with ether, and afterwards thoroughly dried by exposing it to the air on filter paper. 10 grams of meta-nitraniline gave 12 grams of the nitrate of the diazo-compound.

Meta-nitro-diazo-benzene nitrate crystallises in small grains, which at first are almost white, but soon become brown when exposed to the air. It is very soluble in water. It changes but slightly, even when exposed to the air for twenty-four hours. It explodes by concussion, though not violently.

Preparation of meta-nitro-diazo-benzene sulphate.—The sulphate was made as follows: 10 grams meta-nitraniline were placed in a flask, and a slight excess of concentrated sulphuric acid added, and a few cubic centimeters of water. After stirring for some time until the change to the white sulphate was complete, 100 cc. of ordinary alcohol were added, and the oxides of nitrogen passed into the liquid until they were no longer absorbed. The liquid contents of the flask were then quickly poured upon a filter. The filtrate was cooled by means of a freezing mixture, and ether added, when the diazo-compound was soon thrown down as a granular powder. 10 grams meta-nitraniline yielded 11.5 grams of the sulphate.

Meta-nitro-diazo-benzene sulphate appears in perfectly white granular crystals. It is readily soluble in water, and is quite stable. When allowed to stand for some time in a desiccator over sulphuric acid, it became colored a delicate pink; but even after standing for several days, there appeared to be no material decomposition. It is not decomposed by concussion. When heated by a free flame, it deflagrates and swells up, leaving a black residue.

Decomposition of meta-nitro-diazo-benzene nitrate by alcohol.—This was treated in the same way as the sulphate of ortho-nitro-diazo-benzene. When the temperature of the water-bath reached 70°, the decomposition began, and it was completed at 75°. Alde-

hyde was given off freely, and a reddish liquid resulted. After the action was over, the excess of alcohol was distilled off, water added, and the contents of the flask distilled in steam. The only product of decomposition which could be isolated was the nitro-benzene, which passed over with the water-vapor. A tarry residue remained in the flask. From 46 grams of the nitrate 15 grams nitro-benzene were obtained, the yield being 55 per cent. of the theoretical.

Decomposition of meta-nitro-diazo-benzene sulphate by alcohol.—Decomposition began at 65° and was completed at 70°. Aldehyde was given off freely. Nitro-benzene was carried over with steam, and no other product was isolated. 22 grams of the sulphate yielded 7 grams nitro-benzene, a yield of about 66 per cent.

The decomposition of the nitrate and of the sulphate by water and in toluene was studied, but definite products could not be obtained.

Preparation of para-nitro-diazo-benzene nitrate.—In consequence of the ease with which the diazo-amido-compound is formed when para-nitraniline nitrate is treated with nitrous acid, considerable difficulty was experienced in preparing the diazo-compound. By working as described below, the compound is easily obtained. 20 grams para-nitraniline were placed in a flask with 60 cc. dilute nitric acid. On gently heating, the nitrate was formed. The contents of the flask were then cooled by ice, and treated with a rapid current of the oxides of nitrogen. Whenever a precipitate of the diazo-amido-compound began to form, the flask was removed for an instant from the ice-water. In the course of twenty-five minutes the end of the reaction was reached, and this was shown by a change of color of the solution to a dingy green, and by the escape of oxides of nitrogen. After cooling in a freezing mixture of ice and hydrochloric acid, the liquid was quickly filtered by the aid of the pump. To the thoroughly cooled liquid about 250 cc. absolute alcohol and 150 cc. anhydrous ether were added, and the flask constantly shaken in the freezing mixture. In a few minutes the needle-shaped crystals of the diazo-compound separated out. These were quickly filtered and washed on the filter, first with absolute alcohol, then with anhydrous ether, and spread out on filter paper. 20 grams of para-nitraniline gave 16 grams of the nitrate.

Para-nitro-diazo-benzene nitrate forms long needle-like crystals

of a beautiful silky lustre. When first formed it is white, but it soon becomes yellow by exposure to the air. It explodes violently when heated or struck. It is readily soluble in water, and almost insoluble in alcohol and in ether.

Decomposition of para-nitro-diazo-benzene nitrate by alcohol.— This compound was treated with alcohol in the same way as the ortho- and the meta-compounds. The decomposition began at 70° and was rapidly completed at 75°. After the decomposition was finished, the alcohol was distilled off and the residue distilled with water-vapor. The only product isolated was nitro-benzene, which was recognised by its odor, specific gravity, and boiling point. From 40 grams of the diazo-compound 16 grams nitro-benzene were obtained, a quantity which represents a yield of 70 per cent.

Experiments on the conduct of para-nitro-diazo-benzene nitrate when treated with water and with toluene gave unsatisfactory results. Definite products could not be obtained.

The above experiments are of interest as showing that the presence of the nitro-group in any one of the three possible positions relatively to the diazo-group causes the reaction with alcohol to take place in a different way from that in which it takes place when the nitro-group is not present. At the same time it will be observed that the influence exerted by this group is different from that exerted by the methyl-group.

Experiments with the Diazo-benzoic Acids.

Decomposition of ortho-diazo-benzoic acid nitrate by alcohol.— The nitrate was made by the method described by Griess.[1] From 10 grams of ortho-amido-benzoic acid 12 grams of the nitrate of the diazo-compound were obtained. On heating the nitrate with absolute alcohol on the water-bath, decomposition began at 60° and was completed at 70°. The alcohol was distilled off, the residue diluted with water and distilled in steam. An oil which was heavier than water passed over. The oil was separated from the water and dried over calcium chloride, when it was found to boil at 213°. This fact, taken together with the characteristic odor of the oil, showed it to be ethyl benzoate. Further, when boiled with potassium hydroxide it was saponified, yielding benzoic acid with

[1] Ber. d. deutsch. Ges. **9**, 1653.

all its characteristic properties. A small quantity of benzoic acid was obtained from the contents of the flask from which the ethyl benzoate had been expelled by steam, but the ethyl benzoate was formed in by far the larger quantity. Of the latter, 8 grams were obtained from 24 grams of the diazo-compound in the form of nitrate, a yield of 53 per cent. of the theoretical.

Decomposition of ortho-diazo-benzoic acid nitrate in toluene.— 8 grams of the nitrate were heated in toluene on a water-bath. No signs of decomposition were noticed until the boiling point of water was reached; and at this point the action set up was so violent as to necessitate removal from the bath; and for some time after the removal it continued vigorously. Meantime the flask was constantly shaken, and, when the action ceased, it was again heated until the decomposition was finished. Barium carbonate in suspension was then added and the whole thoroughly shaken. The toluene was separated and tested for substances in solution, but nothing was found. The water solution was boiled to free it from all toluene, and then filtered. After acidifying, a precipitate was formed which, after being repeatedly boiled with bone-black and recrystallised, appeared in the form of long, yellowish, needle-shaped crystals which melted at 228°. The solution of this acid gave a blood-red precipitate with ferric chloride. These are the properties ascribed by Griess[1] to unsymmetrical nitro-salicylic acid, $C_6H_3\begin{cases}COOH & (1)\\ OH & (2).\\ NO_2 & (4)\end{cases}$

The amount of the substance obtained was not sufficient for a careful comparison, but there can be little doubt that it is the acid described by Griess. This transformation is analogous to that of diazo-benzene nitrate into ortho-nitro-phenol,[2] and that of diazo-benzene sulphate into para-phenol-sulphonic acid,[3] under the same conditions.

Decomposition of meta-diazo-benzoic acid sulphate by alcohol.— The sulphate was prepared by the method of Griess,[4] 12 grams being obtained from 10 grams of the metamido acid. 62 grams of the sulphate were decomposed in absolute alcohol in the manner described in the experiment with the ortho-compound. The decomposition began when the temperature of the bath indicated the boiling point of alcohol. If it was lowered to 70° the action

[1] Ber. d. chem. Ges. **11**, 1730.
[2] This Journal **9**, 391.
[3] Ibid. **9**, 393.
[4] Ber. d. chem. Ges. **9**, 1655.

stopped. It was necessary to keep it at about 78°, at which point the action took place rapidly. A faint odor of aldehyde was noticed. The excess of alcohol was distilled off after the reaction was finished; the residue was then diluted with water and the contents of the flask distilled in steam. An oil which was heavier than water passed over. The liquid left in the distilling flask was boiled with bone-black, filtered, evaporated, and allowed to stand, but only a small quantity of a tarry oil was thus obtained. The chief product formed was the volatile oil which passed over on distilling with steam. This was found to boil at 213°, and on saponification it gave benzoic acid. The properties of the substance showed conclusively that it is ethyl benzoate. From 62 grams of the sulphate 24 grams of ethyl benzoate were obtained, the yield being 63 per cent. of the theoretical. According to these experiments, therefore, the sulphate of meta-diazo-benzoic acid acts in essentially the same way as the nitrate of ortho-diazo-benzoic acid. Fittica states[1] that when meta-diazo-benzoic acid sulphate is decomposed by alcohol, benzoic acid is obtained. When meta-diazo-benzoic acid sulphate is heated in toluene, decomposition takes place at the temperature of the water-bath, but it was not found possible to isolate any definite substance from the products.

Decomposition of para-diazo-benzoic acid nitrate by alcohol.— The nitrate was made as recommended by Griess.[2] When thrown down suddenly, the compound has much the appearance of light brown sugar. When crystallised from a comparatively dilute solution, the crystals appear as needles, while, when deposited slowly from a considerable quantity of alcohol and ether, it forms thick, colorless, monoclinic prisms, terminated by an orthodome. It is very stable for a diazo-compound, and does not undergo decomposition on standing for several days exposed to the air. Further, it is not decomposed by concussion, but it explodes when heated. It is easily soluble in water, and insoluble in absolute alcohol and in ether. A nitrogen determination of the nitrate was made by boiling with water and collecting the nitrogen given off, with the following result:

	Calculated for $C_6H_4\langle^{COOH}_{N_2-NO_3}$.	Found.
N_2	11.60	11.83

24 grams of the nitrate were decomposed as already described.

[1] Ber. d. chem. Ges. **11**, 1209. [2] Ann. Chem. (Liebig), **120**, 126.

The decomposition began at 74° and was complete when the temperature had reached 78°. On treating the resulting liquid as was done in the case of the ortho- and meta-compounds, only a small quantity of oil passed over with water-vapor. This proved to be ethyl benzoate. The principal product was, however, not volatile, and crystallised out of the liquid in the distilling flask. This substance sublimed, forming white leaflets. It was found to be difficultly soluble in water, both cold and hot, and easily soluble in alcohol. It melted at 196°. These properties show that the substance is the para-ethoxy-benzoic acid described by Fuchs[1] and by Ladenburg and Fitz.[2] From 24 grams of the nitrate decomposed, between 9 and 10 grams of the acid were obtained, representing a yield of about 50 per cent. of the theoretical, while only about 2 grams of benzoic acid were obtained. The reaction in this case, then, takes place mainly according to the following equation:

$$C_6H_4\begin{cases}COOH\\N_2-NO_3\end{cases}+C_2H_5OH=C_6H_4\begin{cases}COOH\\OC_2H_5\end{cases}+N_2+HNO_3.$$

The identity of the acid was proved by a comparison of some of its salts with those described by Ladenburg and Fitz.[2]

The *barium salt*, made by adding barium chloride to a neutral solution of the ammonium salt of the acid, formed very slowly in groups of white scale-like crystals, which were soluble to some extent in cold water and easily in hot water.

The *ammonium salt* is very soluble in water, and was obtained only from concentrated solutions. It crystallises in small white tabular crystals.

The *silver salt*, made by adding silver nitrate to a neutral solution of the ammonium salt, came down at first as a white voluminous precipitate, quite insoluble in cold water and difficultly soluble in hot water. It crystallised from water in needles.

The *lead salt*, made by adding lead acetate to the neutral ammonium salt, was thrown down at once as a white voluminous precipitate, much less soluble in cold water than the barium salt.

The *calcium salt*, made by adding calcium chloride in solution to the neutral ammonium salt, formed very slowly, and only from concentrated solution. The salt formed white needle-like crystals, quite soluble in water.

Decomposition of para-diazo-benzoic acid nitrate by methyl alcohol.—The decomposition began at 57° and was complete at

[1] Ber. d. chem. Ges. **2**, 625. [2] Ann. Chem. (Liebig), **141**, 255.

62°. The product obtained was anisic or para-methoxy-benzoic acid, $C_6H_4<^{COOH}_{OCH_3}$. Its melting point was found to be 185°. From 10 grams of the nitrate about 4 grams of the acid were obtained.

Decomposition of para-diazo-benzoic acid nitrate by propyl alcohol.—The decomposition began when the temperature of the bath reached 78° and was complete at 85°. The chief product formed was a crystallised compound which proved to be para-propoxy-benzoic acid, $C_6H_4<^{COOH}_{OC_3H_7}$. About 6 grams were obtained from 15 grams of the nitrate.

Para-propoxybenzoic acid.—The acid was purified by treatment with bone-black and crystallisation from dilute alcohol. It crystallises in lustrous plates having much the appearance of fish scales. It is practically insoluble in cold water, and with difficulty in hot water; easily in alcohol. It melts at 141.5°–142.5°. It sublimes in thin white plates. An analysis gave the following results:

0.2442 gram substance gave 0.5991 gram CO_2 and 0.145 gram H_2O.

	Calculated for $C_6H_4<^{COOH}_{OC_3H_7}$.	Found.
C	66.67	66.91
H	6.67	6.59
O	26.66	...
	100.00	

Barium para-propoxybenzoate, made by adding barium chloride to a solution of the neutral ammonium salt, was thrown down as a white flocculent precipitate, somewhat soluble in cold water, readily soluble in hot water. An analysis gave the following result:

.09 gram substance gave 0.0421 gram $BaSO_4$.

	Calculated for $\left[C_6H_4<^{COO}_{OC_3H_7}\right]_2Ba + H_2O$.	Found.
Ba	26.97	26.70

The *silver salt* was made by adding silver nitrate to the neutral ammonium salt. It appeared in the form of a white curdy precipitate, insoluble in cold water, and with difficulty in hot water.

Groups of small needle-shaped crystals were deposited from the solution in water.

The *lead salt*, made by adding lead acetate to the solution of the ammonium salt, was thrown down as a white curdy precipitate, almost insoluble in cold water, readily soluble in hot water. From the solution in hot water it crystallises in small feathery crystals.

The *calcium salt*, made by adding calcium chloride to the solution of the ammonium salt, appeared as a white flocculent precipitate, slightly soluble in cold water, and very readily in hot water. It crystallises in small flocculent crystals from its solution in hot water.

Decomposition of para-diazo-benzoic acid nitrate by water.—The decomposition took place between 80° and 90°. The contents of the flask were filtered to remove a small quantity of a tarry substance, then boiled with bone-black, filtered and allowed to crystallise. In this way, after several crystallisations, two crystallised products were obtained. The one which was formed in larger quantity appeared in granular yellowish crystals melting at 178°. The properties are those of the nitro-oxybenzoic acid described by Max Gruber.[1] Gruber expresses the opinion that his acid is m-nitro-p-oxybenzoic acid, $C_6H_3\begin{cases}COOH & (1)\\ NO_2 & (3)\\ OH & (4)\end{cases}$. On the other hand, the acid of this constitution has been shown by Griess[2] to melt at 185°. The quantity at our disposal was so small as to prevent further purification, and the constitution of the acid cannot be regarded as satisfactorily determined.

The second product of the decomposition of para-diazo-benzoic acid nitrate with water was shown to be para-oxybenzoic acid. It was formed in very small quantity in our experiments, whereas, according to Griess,[3] it is the principal product of this decomposition.

Decomposition of para-diazo-benzoic acid nitrate in toluene.—This decomposition began at 90° and was rapidly completed at the boiling point of water. The action was accompanied by an evolution of nitrogen and the formation of tarry products. After the action was over, the solution in toluene was shaken up with water and barium carbonate, and the toluene then drawn off. A

[1] Ber. d. chem. Ges. **12**, 520. [2] Ber. d. chem. Ges. **20**, 408.
[3] Ann. Chem. (Liebig), **120**, 126.

barium salt was found to be in the water solution. After purification of the salt, the acid was separated, and was found to be identical with the nitro acid obtained on decomposing in water. The reaction in toluene is therefore represented in this way:

$$C_6H_4\begin{cases}COOH\\N_2—NO_3\end{cases} = C_6H_3\begin{cases}COOH\\NO_2\\OH\end{cases} + N_2.$$

Comparison of the results obtained in the decomposition of the diazo-benzoic acids by alcohols with those obtained by Griess.—As has been stated, the object of the investigation to which the present communication relates is to determine under what conditions diazo-compounds are decomposed by alcohol in such way that hydrogen takes the place of the diazo-group, and what conditions are favorable to the formation of phenol ethers. This subject had never, so far as appears from the literature, been investigated by Griess, nor does it appear that this chemist ever recognised the possibility of the formation of phenol ethers as a result of the decomposition of diazo-compounds. After the last communication on the subject by one of us (R.) and Orndorff,[1] and after the work described in this paper was completed, Griess[2] published a paper in which he gives the results of experiments on the decomposition of the diazo-benzoic acids by alcohol. In this paper he says that he has long been engaged in this investigation, and that he proposes to continue it. Unfortunately for science this promise was not to be kept, as he died soon afterwards. We should not have done the work described in this paper had Griess' paper been published before we undertook it, and we certainly should not publish our results now, were it not for the fact that in some respects they differ markedly from those described by Griess.

According to this chemist, when ortho-diazo-benzoic acid sulphate is decomposed by alcohol, it is completely converted into benzoic acid, which is obtained directly as such; meta-diazo-benzoic acid sulphate gives benzoic acid and meta-ethoxy-benzoic acid; and para-diazo-benzoic acid sulphate acts like the meta-compound, giving both benzoic acid and para-ethoxy-benzoic acid. We used the nitrate of ortho-diazo-benzoic acid, and obtained ethyl benzoate, with only a very small quantity of benzoic acid. It is possible that the nitrate and sulphate act differently. With the sul-

[1] This Journal **9**, 387.

[2] Ber. d. chem. Ges. **21**, 978.

phate of meta-diazo-benzoic acid we obtained results quite different from those described by Griess. We obtained no benzoic acid, and no ethoxy-benzoic acid, but only ethyl benzoate. We are entirely at a loss to explain the difference, as the work, as nearly as can be judged, was carried on in the same way in both investigations. It would appear, at least, that slight changes in the conditions may cause a very marked difference in the results. Passing now to the para-series, our results with the nitrate are more nearly in accordance with those obtained by Griess with the sulphate, than those in the ortho- and meta-series. We obtained anisic acid with methyl alcohol, para-ethoxy-benzoic acid with ethyl alcohol, and para-propoxybenzoic acid with propyl alcohol. In the decomposition with ethyl alcohol, in which we used a considerably larger quantity of the diazo-compound than in the other cases, a small quantity of ethyl benzoate was obtained.

Influence of the composition, and of the position of groups in determining the course of the action of alcohols on diazo-compounds. —From the results obtained in the study of the decomposition of the three diazo-compounds derived from the toluidines, the conclusion was reached that a methyl-group in the para-position to a diazo-group is favorable to the replacement of this group by hydrogen by treatment with alcohol. Considering now the results described in this paper, it is clear that the influence exerted by the nitro-group is different from that exerted by methyl, and apparently carboxyl acts in still another way. The nitro-group influences the diazo-group whether in the ortho-, the meta-, or the para-position, so that it is replaced by hydrogen. This reaction can only be accounted for by assuming that it is due to the influence of the nitro-group, for it has been shown that when diazobenzene itself is decomposed by alcohol, that is, when the nitro-group is not present in the molecule, the reaction with alcohol takes, for the most part, the other direction. Finally, as regards the influence of carboxyl, our results seem to show that it is exerted upon the ortho- and meta-diazo-groups, causing them to be replaced by hydrogen, while the diazo-group in the para-position undergoes the same reaction as if the carboxyl were not present in the compound. The conclusion is therefore justified that both the position and the character of the groups in the molecule of diazo-compounds exert an influence on the decomposition of the compounds by alcohol.

ON *o*-SULPHOBENZOIC ACID AND SOME OF ITS DERIVATIVES.

By Ira Remsen and A. R. L. Dohme.

Preparation and Properties of o-Sulphobenzoic Acid.

We have found that this acid can easily be prepared from commercial saccharin in the following way: The commercial product, which, as will be shown in a later article by Mr. W. M. Burton and one of us (R.), consists mainly of benzoic sulphinide and *p*-sulphamine-benzoic acid in nearly equal quantities. When the mixture is boiled with dilute hydrochloric acid, the sulphinide is converted into the acid ammonium salt of *o*-sulphobenzoic acid, while the *p*-sulphamine-benzoic acid is not changed by this treatment. As the acid ammonium salt is easily soluble in water, and *p*-sulphamine-benzoic acid is difficultly soluble, it is only necessary to filter and evaporate to dryness in order to get the ammonium salt. After purification this is dried, and then treated with twice its weight of phosphorus pentachloride. Reaction takes place spontaneously and the mass becomes semi-liquid. When the reaction is complete, the mixture is thoroughly washed with cold water, the chloride remaining as a heavy yellowish oil undissolved. The chloride is then boiled with water until it is decomposed, and the resulting liquid is evaporated to complete dryness to drive off all the hydrochloric acid. The reactions are all quantitative, and the acid thus obtained is pure.

The acid is very easily soluble in water. If its solution is evaporated to a syrupy consistency, it crystallises in long, lathe-shaped, colorless, orthorhombic crystals, which sometimes attain the length of several inches. The faces of the crystals are always etched, a fact which renders a crystallographic examination of them impossible. The accompanying drawing (Fig. 1) shows their general appearance. They are orthorhombic, and usually exhibit only the forms given, viz. ∞ P$\breve{\infty}$, ∞ P

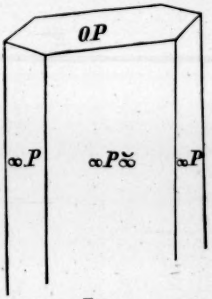


Fig. 1.

and oP, though sometimes there is a macropinacoid ($\infty P\bar{\infty}$) truncating the remaining edges, in which two prismatic faces (∞P) meet. There is a decided cleavage parallel to the best developed face ($\infty P\bar{\infty}$), the brachypinacoid. The acid is slightly hygroscopic. It is very easily soluble in hot and in cold water, but insoluble in ether. It melts at 68°–69°, and solidifies on cooling to a white crystalline mass. If heated for some time at 130°, however, and then allowed to cool, it is found to melt at 130°. This, as will be shown, is due to the fact that the acid when deposited from water solutions contains four molecules of water of crystallisation, and that, when heated at 130°, it becomes anhydrous. Further, when the crystallised hydrated acid is allowed to lie over sulphuric acid in a desiccator for a long time, it loses its water and becomes anhydrous. The analysis of the acid deposited from water gave the following figures:

I. 0.2771 gram gave 0.3046 gram CO_2 and 0.1247 gram H_2O.
II. 0.2855 gram gave 0.3180 gram CO_2 and 0.1295 gram H_2O.
III. 0.3320 gram gave 0.2856 gram $BaSO_4$.
IV. 0.2510 gram gave 0.2083 gram $BaSO_4$.
V. 0.1563 gram lost 0.04076 gram H_2O when heated to 125°.
VI. 0.1278 gram lost 0.0334 gram H_2O when heated to 125°.

	Calculated for $C_6H_4<^{COOH}_{SO_3OH}+4H_2O$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	30.66	29.98	30.38	...	...	...	...
H	5.11	5.	5.04	...	...	...	...
O		...	...	...	...	...	...
S	11.68	...	...	11.81	11.39	...	...
H_2O	26.28	...	...	...	...	26.08	26.13

The combustions were made with lead chromate. The sulphur estimations were made by Pearson's method.[1] In determining the water of crystallisation, it was found that three molecules of water are given off at 100°, one half a molecule at 120°, and the last half molecule at about 125°–128°.

When the crystallised acid is kept for some time at 130° a sublimate is formed, which consists of long, thin, white needles, resembling phthalic anhydride. This was supposed to be the anhydride of *o*-sulphobenzoic acid, but analysis showed that it is the acid with two molecules of water.

[1] Ztschr. anal. Chem. **9**, 271.

I. 0.1322 gram substance gave 0.1732 gram CO_2 and 0.0549 gram H_2O.

II. 0.0903 gram substance gave 0.1179 gram CO_2 and 0.0336 gram H_2O.

	Calculated for $C_6H_4<^{COOH}_{SO_3OH}+2H_2O$.	Found. I.	Found. II.
C	35.29	35.73	35.61
H	4.20	4.61	4.13

The fact that these results, as well as those obtained in the analysis of the acid with four molecules of water, do not more closely agree with the theory is satisfactorily accounted for by the easy solubility of the acid, and hence the difficulty of getting it in perfectly pure condition, and further by the method of forming the sublimed acid. As it is shown that when the hydrated acid is heated for a sufficient length of time to 125°–128° it loses all its water, it is evident that the sublimed acid is the result of an act of dissociation and recombination of the anhydrous acid with water.

o-Sulphobenzoic Anhydride, $C_6H_4<^{CO}_{SO_2}>O$.

From the experiments above described it appears that even though *o*-sulphobenzoic acid when heated to a sufficiently high temperature may break down into the anhydride and water, these reunite and form a sublimate of the acid. In order to prevent this, the acid, from which the water of crystallisation had been driven off by continued heating at 125° in an air-bath, was mixed with phosphorus pentoxide and this mixture heated. The apparatus used consisted of a small flask of about 75 cc. capacity, through the stopper of which a piece of wide glass tubing a foot long and of an internal diameter of three quarters of an inch was introduced so that about an inch of the tube extended below the lower surface of the stopper into the flask. The mixture of the acid and phosphorus pentoxide was put into the flask and this then introduced into a bath of sulphuric acid, so that the entire body of the flask was immersed and the lower end of the tube reached nearly to the level of the sulphuric acid in the bath. The bath is kept at 130° for several hours, and during this time lustrous, transparent needles and rhombs collect upon and within the lower part of the tube. These crystals sometimes reach the length of an inch. When first taken out they are transparent and

limpid like calcite, which they closely resemble, except that they are probably monoclinic. The melting point is 128°. When exposed to the air the crystals quickly become opaque and white. The analysis of the clear crystals just taken from the tube gave the following results:

I. 0.1166 gram substance gave 0.1964 gram CO_2 and 0.0253 gram H_2O.

II. 0.0809 gram substance gave 0.1361 gram CO_2 and 0.0173 gram H_2O.

III. 0.2205 gram substance gave 0.2787 gram $BaSO_4$ (by Pearson's method).

IV. 0.2442 gram substance gave 0.3049 gram $BaSO_4$ (by Pearson's method).

	Calculated for $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>O$.	Found. I.	II.	III.	IV.
C	45.65	45.94	45.88	...	...
H	2.17	2.41	2.38	...	...
S	17.39	...	...	17.35	17.14

These results leave no room for doubt that the substance is the anhydride of *o*-sulphobenzoic acid. It was stated above that when the anhydride is left exposed to the air the crystals soon become opaque. Analysis showed that the substance thus formed is the anhydrous acid $C_6H_4<\begin{matrix}COOH\\SO_2OH\end{matrix}$. The following figures were obtained:

0.1635 gram substance gave 0.2476 gram CO_2 and 0.0456 gram H_2O.

	Calculated for $C_6H_4<\begin{matrix}COOH\\SO_2OH\end{matrix}$.	Found.
C	41.58	41.30
H	2.97	3.10

Salts of o-Sulphobenzoic Acid.

Neutral Barium o-Sulphobenzoate, $C_6H_4<\begin{matrix}COO\\SO_2O\end{matrix}>Ba + 2H_2O$. —This was made by boiling a solution of the acid ammonium salt with pure barium carbonate until no more ammonia was detected in the escaping steam. It crystallises from fairly concentrated

solutions in beautiful colorless prisms, which are frequently arranged in tufts, and are then elongated in one direction so that they look like needles. Its crystalline form is shown in Fig. 2. It is not quite as easily soluble in water as most of the other salts of the acid. It does not lose all its water of crystallisation until heated to 190°. An optical examination gave the following results:

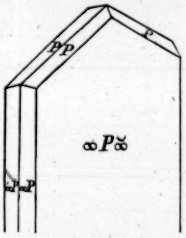


FIG. 2.

System orthorhombic.—Crystals elongated in the direction of the principal axis, and tabular in the plane of the principal and brachy axes. Cleavage parallel to the best developed face, the brachypinacoid ($\infty P\bar{\infty}$).—Axial ratio a : b : c = .5106 : 1 : .6416. The angles measured are:

$$\infty P \wedge \infty P = 125° 55'$$
$$\infty P \wedge \infty P\bar{\infty} = 117° 6'$$
$$P \wedge \infty P\bar{\infty} = 122° 41'$$
$$P \wedge P = 114° 35'$$

The extinction is parallel; the plane of the optic axes lies in the brachypinacoid, and the double refraction is weak.

The analysis gave the following results:

I. 0.21935 gram lost 0.0213 gram at 190° and gave 0.1371 gram $BaSO_4$.

II. 0.3175 gram lost 0.0318 gram at 190° and gave 0.1968 gram $BaSO_4$.

	Calculated for $C_6H_4<^{COO}_{SO_2O}>Ba + 2H_2O$.	Found. I.	II.
Ba	36.73	36.75	36.45
H_2O	9.65	9.71	10.02

Acid Barium o-Sulphobenzoate, $\left(C_6H_4<^{COOH}_{SO_2O}\right)_2 Ba + 4\frac{1}{2}H_2O$. —This salt was described by Remsen and Fahlberg. They found that it contained two molecules of water of crystallisation, while the analyses given below show that the salt as prepared by us contained four and a half molecules. It was made by boiling the neutral salt with concentrated hydrochloric acid. A mixture of equivalent quantities of barium chloride and the acid salt was thus

obtained, and these were separated by repeated crystallisations. The salt crystallises in long, thin, white, silky needles from moderately concentrated solutions. The analysis gave the following results:

I. 0.2416 gram lost 0.0317 gram and gave 0.0916 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{matrix}COOH\\SO_2O\end{matrix}\right)_2Ba+4\frac{1}{2}H_2O$.	Found.
Ba	22.10	22.29
H_2O	13.07	13.12

Neutral Calcium o-Sulphobenzoate, $C_6H_4<\begin{matrix}COO\\SO_2O\end{matrix}>Ca+5H_2O$. —This was made by treating finely powdered Iceland spar with a solution of the free acid. After standing for some time over sulphuric acid it crystallises from very concentrated solutions in large, beautiful, colorless, monoclinic prisms, which are, however, much shorter and thicker than those of the neutral barium salt. They are quite efflorescent, and it was therefore impossible to measure the angles. It is more soluble than the barium salt. The analysis gave the following results:

I. 0.2152 gram lost 0.0585 gram at 150° and gave 0.0886 gram $CaSO_4$.

II. 0.2016 gram lost 0.0549 gram at 150° and gave 0.0838 gram $CaSO_4$.

	Calculated for $C_6H_4<\begin{matrix}COO\\SO_2O\end{matrix}>Ca+5H_2O$.	Found. I.	Found. II.
Ca	12.12	12.11	12.22
H_2O	27.27	27.18	27.23

Acid Calcium o-Sulphobenzoate, $\left(C_6H_4<\begin{matrix}COOH\\SO_2O\end{matrix}\right)_2Ca+6H_2O$. —This was made by mixing solutions of equivalent quantities of the free acid and of the neutral salt. It crystallises in short, colorless, monoclinic plates, and is very soluble in water. The analysis gave the following results:

0.1683 gram lost 0.0330 gram at 125° and gave 0.0423 gram $CaSO_4$.

	Calculated for $\left(C_6H_4<\begin{matrix}COOH\\SO_2O\end{matrix}\right)_2Ca+6H_2O$.	Found.
Ca	7.27	7.39
H_2O	19.64	19.61

Neutral Ammonium o-Sulphobenzoate, $C_6H_4<\begin{matrix}COONH_4\\SO_2ONH_4\end{matrix}$. —This was made by neutralising a solution of the acid ammonium salt

with ammonia. It crystallises from quite concentrated solutions in colorless, short, thick, lozenge-shaped crystals. The form of the crystals is represented in Fig. 3. An optical examination gave the following results:

System orthorhombic.—The faces $\infty P\bar{\infty}$, $P\bar{\infty}$ and ∞P are equally developed, causing the crystal to assume the lozenge shape. Axial ratio a : b : c = .8904 : 1 : .7125. The angles measured are:

$$\infty P\bar{\infty} \wedge P\bar{\infty} = 128° 40'$$
$$\infty P \wedge \infty P = 83° 23'$$
$$\infty P \wedge \infty P\bar{\infty} = 137° 48'$$

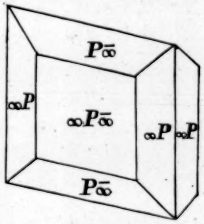


FIG. 3.

On some of the crystals the basal plane occurs and truncates the edge between the two dome faces ($P\bar{\infty}$). The reflections are not very good.

The ammonia was determined by Kjeldahl's method, with the results below given:

I. 0.1213 gram gave 0.0173 gram NH_3.

II. 0.1684 gram gave 0.02397 gram NH_3.

	Calculated for $C_6H_4{<}^{COONH_4}_{SO_3ONH_4}$.	Found. I.	Found. II.
NH_3	14.41	14.26	14.23

Acid Ammonium o-Sulphobenzoate, $C_6H_4{<}^{COOH}_{SO_3ONH_4}$. — This salt, as has been repeatedly stated, is formed when benzoic sulphinide is boiled with hydrochloric acid, most readily when the acid is dilute. It has been described and analysed, and its true nature was first recognised by Linn and one of us (R.).[1]

Neutral Potassium o-Sulphobenzoate, $C_6H_4{<}^{COOK}_{SO_3OK} + 2H_2O$.— This was made by neutralising a solution of the acid potassium salt with potassium carbonate. It is more soluble than any of the salts thus far described, and crystallises from very concentrated solutions in concentrically arranged groups of small white needles. An analysis gave the following results:

0.2167 gram lost 0.02397 gram at 180° and gave 0.1190 gram K_2SO_4.

[1] This Journal **11**, 73.

	Calculated for $C_6H_4<^{COOK}_{SO_2OK} + 2H_2O$.	Found.
K	24.84	24.62
H_2O	11.46	11.06

Acid Potassium o-Sulphobenzoate, $C_6H_4<^{COOH}_{SO_2OK}$.—This salt was first described by Remsen and Fahlberg.[1] It is obtained from the mother-liquors of commercial saccharin, of which it forms, as has been found by Burton and one of us, from 6 to 8 per cent. It crystallises very beautifully.

Neutral Silver o-Sulphobenzoate, $C_6H_4<^{COOAg}_{SO_2OAg}$.—This was prepared by boiling a solution of the free acid with an excess of silver carbonate. It is somewhat less soluble than the other salts made. It crystallises well in colorless, short, monoclinic prisms which become dark on exposure to the light. The analysis gave the following results:

I. 0.2177 gram gave 0.1500 gram AgCl.
II. 0.2496 gram gave 0.1720 gram AgCl.

	Calculated for $C_6H_4<^{COOAg}_{SO_2OAg}$.	Found. I.	Found. II.
Ag	51.92	51.81	51.81

Silver-ammonium o-Sulphobenzoate, $C_6H_4<^{COOAg}_{SO_2ONH_4}$. — This was made by dissolving freshly precipitated silver hydroxide in a solution of the acid ammonium salt. It crystallises in beautiful colorless monoclinic prisms, which closely resemble those of the neutral silver salt. It turns dark if exposed for some time to the light, and decomposes when heated above 130°.

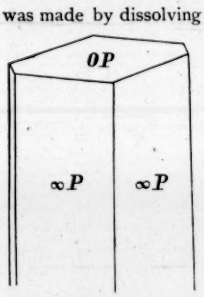


FIG. 4.

An optical examination gave the following results:

System monoclinic.—$\beta = 128° 27'$.—Axial ratio a : b : c = .67228 : 1 : —.[2] The most common forms are oP and ∞P, while less frequently a small clinopinacoidal face was observed, as shown in Fig. 4. The angles measured are:

[1] This Journal 1, 429.

[2] The ratio of c to b cannot be determined, for the reason that no pyramidal or dome faces are present upon any of the crystals of this salt.

$$\infty P \wedge \infty P = 124° 27'$$
$$oP \wedge \infty P = 123° 23'$$

The analysis gave the figures below:
0.2687 gram gave 0.1192 gram AgCl.

	Calculated for $C_6H_4<^{COOAg}_{SO_2ONH_4}$.	Found.
Ag	33.13	33.36

Neutral Copper o-Sulphobenzoate, $C_6H_4<^{COO}_{SO_2O}>Cu + 3\frac{1}{2}H_2O$. —The salt was prepared by adding to a solution of the neutral barium salt exactly enough of a solution of copper sulphate to precipitate the barium. It crystallises only from very concentrated solutions, and appears in concentrically arranged groups of fine dark-blue needles. The crystals are quite hygroscopic, and it was hence found difficult to determine the water of crystallisation. Another difficulty which was encountered in making this determination consists in the fact that the salt decomposes at 180° and the last molecule of water is not given off below 170°. The analysis gave the following results:

0.1633 gram lost 0.0309 gram at 170° and gave 0.0312 gram Cu.

	Calculated for $C_6H_4<^{COO}_{SO_2O}>Cu + 3\frac{1}{2}H_2O$.	Found.
Cu	19.37	19.11
H_2O	19.31	18.92

Neutral Magnesium o-Sulphhobenzoate, $C_6H_4<^{COO}_{SO_2O}>Mg + xH_2O$.—This was prepared in the same way as the copper salt. On evaporating the solution the salt is left in the form of a colorless jelly, and it retains this form even after long standing over concentrated sulphuric acid. It is indeed so hygroscopic that unless the sulphuric acid over which it stands is not very concentrated it abstracts water from the acid. It was not analysed.

Chloride of o-Sulphobenzoic Acid, $C_6H_4<^{COCl}_{SO_2Cl}$.— The chloride is easily prepared by treating the acid ammonium salt with twice its weight of phosphorus pentachloride. It is a colorless oil insoluble in water. When boiled with water it is slowly decomposed, yielding *o*-sulphobenzoic acid and hydrochloric acid. It dissolves in absolute alcohol with decomposition, and in absolute

ether without decomposition. From the solution in ether it crystallises in long, thin, orthorhombic prisms which generally lack the terminal planes. The crystals are represented in Fig. 5.

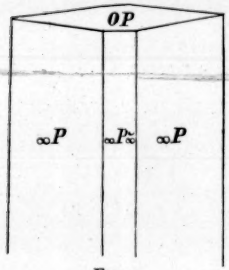


FIG. 5.

An optical examination of the crystals was not possible, because of the unevenness of the planes, due to etching and the action of moisture. The crystals belong to the orthorhombic system, and the forms are ∞ P, ∞ P $\bar{\infty}$, and oP. The crystals are similar to those of the free acid, but have the prism faces (∞P) best developed, while the latter have the pinacoid faces (∞ P $\bar{\infty}$) best developed. The substance melts at 73°. It was analysed by heating it in a pressure-bottle with water until all the oil had disappeared, and then precipitating with silver nitrate. The following results were obtained:

0.1554 gram gave 0.1868 gram AgCl.

	Calculated for $C_6H_4<^{COCl}_{SO_2Cl}$.	Found.
Cl	29.71	29.82

Ethereal Salts of o-Sulphobenzoic Acid.

When the chloride just described is dissolved in cold alcohols the reaction takes place according to the equation:

$$C_6H_4<^{COCl}_{SO_2Cl} + ROH = C_6H_4<^{COOR}_{SO_2Cl} + HCl.$$

If, however, the solution in an alcohol is boiled, the reaction takes place as represented thus:

$$C_6H_4<^{COCl}_{SO_2Cl} + 3ROH = C_6H_4<^{COOR}_{SO_2OH} + 2HCl + R_2O,$$

or the chloride, $C_6H_4<^{COOR}_{SO_2Cl}$, first formed undergoes change as represented in the equation:

$$C_6H_4<^{COOR}_{SO_2Cl} + 2ROH = C_6H_4<^{COOR}_{SO_2OH} + HCl + R_2O.$$

Similar changes were observed in the study of the chloride of *p*-nitro-*o*-sulphobenzoic acid.[1]

[1] See this Journal **11**, 177.

The acid ethereal salts of *o*-sulphobenzoic acid are formed, further, by passing dry hydrochloric acid gas through solutions of the acid in the alcohols. The neutral ethereal salts are made from the silver salts of the acid ethers.

Acid Methyl o-Sulphobenzoate, $C_6H_4<\begin{matrix}COOCH_3\\SO_2OH\end{matrix}$.—This compound is made as above described by boiling the chloride with pure methyl alcohol. It is very easily soluble in water and in alcohol, and cannot be obtained in good crystals. By continued heating on the water-bath with water it is partly saponified.

Barium Methyl o-Sulphobenzoate, $\left(C_6H_4<\begin{matrix}COOCH_3\\SO_2O\end{matrix}\right)_2Ba + 3\frac{1}{2}H_2O$.—This crystallises in concentrically arranged groups of white needles, and is easily soluble in water. The analysis gave these results:

I. 0.1789 gram lost 0.0180 gram at 200° and gave 0.0670 gram $BaSO_4$.

II. 0.1327 gram lost 0.01365 gram at 200° and gave 0.0496 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{matrix}COOCH_3\\SO_2O\end{matrix}\right)_2Ba + 3\frac{1}{2}H_2O$.	Found. I.	Found. II.
Ba	21.75	22.02	21.98
$3\frac{1}{2}H_2O$	10.00	10.06	10.29

Silver Methyl o-Sulphobenzoate, $C_6H_4<\begin{matrix}COOCH_3\\SO_2OAg\end{matrix}$.—This generally separates from water as a colorless, thick jelly, which turns dark when exposed to the light. Once it was obtained in crystals which resemble those of the acid potassium salt of *o*-sulphobenzoic acid. The analysis gave these figures:

I. 0.3683 gram gave 0.1651 gram AgCl.

II. 0.2447 gram gave 0.1096 gram AgCl.

	Calculated for $C_6H_4<\begin{matrix}COOCH_3\\SO_2OAg\end{matrix}$.	Found. I.	Found. II.
Ag	33.43	33.71	33.68

Acid Ethyl o-Sulphobenzoate, $C_6H_4<\begin{matrix}COOC_2H_5\\SO_2OH\end{matrix}$. — This closely resembles the corresponding methyl salt. Only the barium salt could be obtained in crystals.

Barium-ethyl o-Sulphobenzoate, $\left(C_6H_4<\begin{matrix}COOC_2H_5\\SO_2O\end{matrix}\right)_2Ba + 4H_2O$, crystallises in groups of colorless needles arranged like rosettes.

I. 0.1790 gram lost 0.0205 gram at 190° and gave 0.0636 gram $BaSO_4$.

II. 0.2138 gram lost 0.0240 gram at 200° and gave 0.0721 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{matrix}COOC_2H_5\\SO_2O\end{matrix}\right)_2Ba+4H_2O$	Found. I.	II.
Ba	20.54	20.89	19.83
H_2O	10.79	11.45	11.23

Dimethyl o-Sulphobenzoate, $C_6H_4<\begin{matrix}COOCH_3\\SO_2OCH_3\end{matrix}$. — When silver-methyl *o*-sulphobenzoate is heated with methyl iodide in a pressure-bottle at 100° the dimethyl ethereal salt is obtained. By treating with absolute ether and filtering off the silver iodide, the product separates as a colorless jelly.

Diethyl o-Sulphobenzoate is made in the same way as the dimethyl compound, which it resembles.

Ethyl-methyl o-Sulphobenzoate, $C_6H_4<\begin{matrix}COOC_2H_5\\SO_2OCH_3\end{matrix}$. — This compound is made by treating silver-ethyl *o*-sulphobenzoate, $C_6H_4<\begin{matrix}COOC_2H_5\\SO_2OAg\end{matrix}$, with methyl iodide. It forms a colorless jelly.

Methyl-ethyl o-Sulphobenzoate, $C_6H_4<\begin{matrix}COOCH_3\\SO_2OC_2H_5\end{matrix}$.—This is made like the preceding compound, which it resembles and with which it is isomeric.

Decomposition of the Ethereal Salts by means of Water and Alcohol.—The properties of the four compounds just described are so much alike that the compounds themselves cannot be distinguished from one another. There is no difficulty, however, in distinguishing between them when they are treated with water or with alcohol. The result of this treatment is the breaking off of the alkyl group in combination with the sulphuric acid residue. From the dimethyl ether, therefore, acid methyl *o*-sulphobenzoate was obtained; from the diethyl ether the corresponding ethyl compound. The resulting compounds were easily recognised by means of their barium salts. Further, when the compound, $C_6H_4<\begin{matrix}COOC_2H_5\\SO_2OCH_3\end{matrix}$, is boiled with water or with alcohol, the product is acid ethyl *o*-sulphobenzoate, $C_6H_4<\begin{matrix}COOC_2H_5\\SO_2OH\end{matrix}$. The barium salt was analysed with the following results:

0.1387 gram gave 0.0496 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}COOC_2H_5\\SO_2O\end{smallmatrix}\right)_2Ba + 4H_2O$.	Found.
Ba	20.54	21.03

Finally, the compound, $C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2OC_2H_5\end{smallmatrix}$, which is isomeric with the preceding, yields acid methyl *o*-sulphobenzoate, which was identified by means of the barium salt. The analysis gave these results:

0.1102 gram gave 0.0411 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix}\right)_2Ba + 3\frac{1}{2}H_2O$.	Found.
Ba	21.75	21.93

Action of Phosphorus Pentachloride on Benzoic Sulphinide.

In an investigation on the ethers of benzoic sulphinide, Brackett[1] obtained a product by treating benzoic sulphinide successively with phosphorus pentachloride and methyl alcohol, which he took to be the compound $C_6H_4<\begin{smallmatrix}C(OCH_3)_2\\SO_2\end{smallmatrix}>NH$. As he worked with very small quantities and was not able to complete his investigation, we continued the work in the hope of clearing up the reaction which takes place between benzoic sulphinide and phosphorus pentachloride. The result was to show that the compound obtained by Brackett was the methyl ether of *o*-sulphamine-benzoic acid. The corresponding ethyl ether was also made.

Methyl o-Sulphamine-benzoate, $C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2NH_2\end{smallmatrix}$. — This was made exactly according to the directions given by Brackett,[2] and was found to agree with his description. It melts at 124°–125°. Analyses for sulphur and nitrogen resulted as follows:

I. 0.1681 gram gave 0.1848 gram $BaSO_4$.
II. 0.1628 gram gave 0.18137 gram $BaSO_4$.
III. 0.3479 gram gave 0.3868 gram $BaSO_4$.
IV. 0.20385 gram gave 0.01304 gram N (Kjeldahl's method).
V. 0.16705 gram gave 0.01125 gram N (Kjeldahl's method).

[1] This Journal **9**, 406. [2] Loc. cit.

	Calculated for $C_6H_4<^{COOCH_3}_{SO_2NH_2}$.	Found. I.	II.	III.	IV.	V.
S	14.88	15.09	15.23	14.98	...	...
N	6.51	...	...	...	6.40	6.73

Ethyl o-Sulphamine-benzoate, $C_6H_4<^{COOC_2H_5}_{SO_2NH_2}$.—This compound was made in the same way as the methyl ether. It crystallises in beautiful thistle-shaped aggregates of long, white, silky needles which melt at 84°. It dissolves in hot water somewhat more difficultly than the methyl ether, and it melts to a colorless oil before it dissolves. It is easily soluble in alcohol. The analyses gave these results:

I. 0.2250 gram gave 0.2325 gram $BaSO_4$.

II. 0.1079 gram gave 0.1123 gram $BaSO_4$.

III. 0.13055 gram gave 0.0819 gram N (Kjeldahl's method).

IV. 0.1300 gram gave 0.0821 gram N (Kjeldahl's method).

	Calculated for $C_6H_4<^{COOC_2H_5}_{SO_2NH_2}$.	Found. I.	II.	III.	IV.
S	13.97	14.19	14.29	...	...
N	6.11	...	...	6.27	6.31

This ether is identical with the one obtained by Fahlberg and List[1] by treating benzoic sulphinide in alcohol solution with gaseous hydrochloric acid. By way of confirmation both the methyl and ethyl ethers were made by us by this method, and they were found to be identical with the ethers above described. It appears, therefore, probable that when phosphorus pentachloride and alcohol act upon the sulphinide, these react upon each other thus:

$$CH_3OH + PCl_5 = CH_3Cl + POCl_3 + HCl;$$

and that the hydrochloric acid thus liberated acts upon the sulphinide and alcohol, causing them to unite thus:

$$CH_3OH + C_6H_4<^{CO}_{SO_2}>NH = C_6H_4<^{COOCH_3}_{SO_2NH_2}.$$

The act is plainly analogous to that which takes place when an aqueous solution of hydrochloric acid acts upon the sulphinide, converting it first into *o*-sulphamine-benzoic acid, and then into the acid ammonium salt.

[1] Ber. d. chem. Gesell. **20**, 1596.

Propyl o-Sulphamine-benzoate, $C_6H_4<^{COOC_3H_7}_{SO_2NH_2}$.— This was obtained as a colorless oil which could not be crystallised.

It will be observed that the melting points of the ethers above described become lower in the order methyl, ethyl, propyl.

Action of Aniline and of Ortho- and Paratoluidine on the Ethereal Salts of Sulphamine-benzoic Acid, and on Benzoic Sulphinide.

Anilide of o-Sulphamine-benzoic Acid, $C_6H_4<^{CONHC_6H_5}_{SO_2NH_2}$.— By heating either benzoic sulphinide or methyl *o*-sulphamine-benzoate with aniline, the solid dissolves and in the latter case methyl alcohol escapes. On cooling, the mass solidifies. The product was dissolved in water and acidified with hydrochloric acid, when a white crystalline substance separated. This was recrystallised from hot water, in which it is difficultly soluble. It forms short, white, crescent-shaped needles which melt at 189°. The determinations of sulphur and nitrogen gave the following results:

I. 0.1482 gram gave 0.01476 gram N (Kjeldahl's method).
II. 0.1956 gram gave 0.0194 gram N.
III. 0.2017 gram gave 0.02008 gram N.
IV. 0.1300 gram gave 0.11047 gram $BaSO_4$ by Liebig's method.
V. 0.2022 gram gave 0.17267 gram $BaSO_4$.
VI. 0.1419 gram gave 0.11722 gram $BaSO_4$.

	Calculated for $C_6H_4<^{CONHC_6H_5}_{SO_2NH_2}$.	Found.					
		I.	II.	III.	IV.	V.	VI.
N	10.14	9.96	9.91	9.96	...	...	...
S	11.59	...	...	...	11.67	11.72	11.34

The compound is therefore the anilide of the sulphamine acid, and is formed according to the equations:

$$C_6H_4<^{COOCH_3}_{SO_2NH_2} + NH_2.C_6H_5 = C_6H_4<^{CONHC_6H_5}_{SO_2NH_2} + CH_3OH,$$

$$C_6H_4<^{CO}_{SO_2}>NH + NH_2.C_6H_5 = C_6H_4<^{CONHC_6H_5}_{SO_2NH_2}.$$

When boiled with acetic anhydride the anilide gives an acetyl derivative which can be crystallised from water and then appears in the form of beautiful white, satiny needles.

o- Toluide of o-Sulphaminebenzoic Acid, $C_6H_4<\begin{matrix}CONHC_6H_4CH_3\\SO_2NH_2\end{matrix}$.

—Using *o*-toluidine instead of aniline this compound is formed. It is more soluble in water than the anilide, and crystallises from dilute solutions in radially arranged groups of white needles. One recrystallisation suffices to purify it. It melts at 193°. The analysis gave the following figures:

I. 0.15165 gram gave 0.01442 gram N by Kjeldahl's method.

II. 0.1286 gram gave 0.10147 gram $BaSO_4$ by Liebig's method.

	Calculated for $C_6H_4<\begin{matrix}CONHC_6H_4CH_3\\SO_2NH_2\end{matrix}$.	Found. I.	II.
N	9.66	9.50	...
S	11.03	...	10.84

p- Toluide of o-Sulphamine-benzoic Acid, $C_6H_4<\begin{matrix}CONHC_6H_4CH_3\\SO_2NH_2\end{matrix}$.

—This is very difficultly soluble in water, but easily in alcohol. From the former it crystallises in short white needles which melt at 202°. The analysis resulted as follows:

I. 0.2559 gram gave 0.0239 gram N by Kjeldahl's method.

II. 0.1855 gram gave 0.14897 gram $BaSO_4$ by Liebig's method.

	Calculated for $C_6H_4<\begin{matrix}CONHC_6H_4CH_3\\SO_2NH_2\end{matrix}$.	Found. I.	II.
N	9.66	9.34	...
S	11.03	...	11.03

Action of Phosphorus Pentachloride on Benzoic Sulphinide at Higher Temperatures.

From a large number of experiments it appears that phosphorus pentachloride does not act upon benzoic sulphinide to form a chloride even at the temperature of 175° if the experiment is performed in an open vessel. If, however, the two substances are heated together to 160° in a sealed tube, action takes place. The product obtained appeared at first as a colorless oil. This is easily volatile with water vapor, and can easily be purified by distilling it in this way. On cooling the oil solidifies, forming a mass of long white needles which melt at 43°. Analysis showed that it contained chlorine and nitrogen, but no sulphur. The properties mentioned are those given by Henry[1] for *o*-chlorbenzonitrile, which he obtained by treating salicylamide or the nitrile

[1] Ber. d. chem. Gesell. 2, 493.

with phosphorus pentachloride. That the substance obtained by us is really *o*-chlorbenzonitrile was shown by heating it with dilute hydrochloric acid in a sealed tube, when it is completely converted into *o*-chlorbenzoic acid. This crystallised from water in long, flat, white needles which melted at 136°. The reaction with phosphorus pentachloride then involves the replacement of the sulphone group by chlorine and the elimination of oxygen and hydrogen:

$$C_6H_4\begin{cases}CO\\SO_2\end{cases}NH \qquad C_6H_4\begin{cases}CN\\Cl\end{cases}.$$

We should naturally expect to find that the first result of the action of phosphorus pentachloride would be the formation of a chloride of the formula $C_6H_4\begin{cases}CCl_2\\SO_2\end{cases}NH$, and the breaking down of this compound by loss of hydrochloric acid to the form $C_6H_4\begin{cases}CCl\\SO_2\end{cases}N$. It seems hardly probable, however, in view of the structure of the final product, that the reaction takes place in this way. The reaction is of the same kind as that by which Limpricht and Uslar[1] passed from *m*-sulphamine-benzoic acid to *m*-chlorbenzonitrile. Mr. J. M. Rich is at present engaged in a study of the corresponding para compound, which he has made by treating *p*-sulphamine-benzoic acid with phosphorus pentachloride. Like the isomeric compounds, it is very volatile with water vapor.

JOHNS HOPKINS UNIVERSITY, CHEMICAL LABORATORY, *May*, 1889.

THE DISSOCIATION OF THE SULPHIDES OF CADMIUM AND ZINC BY MEANS OF METALLIC CADMIUM AND ZINC.

BY H. N. MORSE AND J. WHITE, JR.

In a former communication[2] we suggested that the transportation in a current of hydrogen of the oxide of zinc and of the sulphides of zinc and cadmium, which was observed by Deville, was

[1] Ann. Chem. (Liebig) **106**, 35. [2] This Journal **11**, 260.

not due, as he supposed, to a *reduction* with formation of water and the sulphide of hydrogen, and a subsequent decomposition of these compounds by the metals, but rather to a *dissociation* of the oxide and of the sulphides under the influence of the hydrogen, and a reunion of the dissociated constituents of these compounds in other parts of the tube.

The intermediate formation of water and of sulphide of hydrogen, especially the latter, seemed to us improbable, for reasons which were there given. It appeared more probable that the attraction of the hydrogen for the oxygen and the sulphur so diminished the stability of the compounds that they dissociated at the prevailing temperature into their elements; that these, unable to recombine as long as the conditions under which the dissociation was effected were maintained, passed along together until other conditions permitting of their reunion were found.

Representing the two views by equations, we have:

I.

1st. $ZnO + H_2 = H_2O + Zn$
$ZnS + H_2 = H_2S + Zn$
$CdS + H_2 = H_2S + Cd$
} at the lower temperature.

2d. $Zn + H_2O = ZnO + H_2$
$Zn + H_2S = ZnS + H_2$
$Cd + H_2S = CdS + H_2$
} at the higher temperature.

II.

1st. $ZnO + xH_2 = Zn + O + xH_2$
$ZnS + xH_2 = Zn + S + xH_2$
$CdS + xH_2 = Cd + S + xH_2$
} probably at the higher temperature.

2d. $Zn + O + xH_2 = ZnO + xH_2$
$Zn + S + xH_2 = ZnS + xH_2$
$Cd + S + xH_2 = CdS + xH_2$
} probably at the lower temperature.

We then suggested, as probably true, the general proposition that when two substances, one a compound and the other something which has an affinity for one of the constituents of the same, are brought together, the stability of the compound is so diminished that it will dissociate at lower temperatures than in the absence of the substance which exerts an attraction upon one of its constituents, and that recombination cannot take place as long as the conditions resulting in dissociation continue.

Such a fact would accord well with what appears to be the most reasonable explanation of those phenomena which we are accustomed to classify under the names of *mass*, *catalytic*, and *contact* action. Indeed, it would be, according to the circumstances, the *extreme phase* of *mass* or of *catalytic action.* It would also explain, in part at least, certain facts connected with the combination of gases, such as the impossibility of exploding a mixture of certain proportions of oxygen and hydrogen.

The dissociation of chemical compounds by one of their own constituents in the free state is involved in the proposition, and it appeared advantageous to begin the attempt at experimental demonstration at that point, because by so doing we should avoid the doubt which would pertain to the results if the formation of new and intermediate compounds were possible, as in the experiments of Deville.

In the first communication we described the dissociation of the oxides of zinc and cadmium by means of their respective metals. We now have to describe a similar dissociation of the sulphides of the same elements.

The pure sulphides were prepared by dissolving the metals, which had been repeatedly distilled in a vacuum,[1] in hydrochloric acid, and precipitating by sulphide of hydrogen obtained from the sulphide of barium. Acetate of sodium was added to the solution of zinc. The precipitates were washed for several days with water containing sulphide of hydrogen, with use of the filter pump. They were then dried at 100°, and afterwards heated for several hours to about 300° in a current of pure and dry sulphide of hydrogen. Finally, to remove any free sulphur which might be present, they were treated for six hours with sulphide of carbon in a Soxlet's extraction apparatus.

The dissociation of the sulphides was effected by the method which was employed in the dissociation of the oxides; their stability in a vacuum having first been demonstrated by heating the exhausted tubes containing them to a temperature at which the glass softened and collapsed. No signs of volatility could be detected. In all subsequent experiments, mixtures of about 15 grams of the sulphide and about 40 grams of the metal were employed.

The phenomena which presented themselves, when the exhausted

[1] This Journal **10**, 312.

tubes containing the mixture of sulphide and metal were heated in the furnace, were similar to those observed during the dissociation of the oxides. Soon after the metal had fused, a yellowish white film formed upon the interior of the cool portion of the tube just outside of the furnace. This film was supposed to be sulphur, and its appearance in that position is to be explained in the same way as the considerable evolution of free oxygen during the early period of the dissociation of the oxides; that is, while the tube is still comparatively free from the vapors of the metal, the sulphur liberated by dissociation, having a higher rate of diffusion than the metal, would naturally escape, in part, and deposit itself in the locality where the formation of the film was observed. Later in the experiments the appearance of these films changed to that of the sulphides. As the temperature of the mixture rose, a deposit of sulphide was observed to form upon the bottom and the top of the tube in front of the dam. This, as in the case of the oxides, was driven farther forward by the distilling metal, and deposited again as a long line of crystals upon the bottom of the tube. But the sulphides which were deposited in the heated portion of the tube in front of the dam did not, like the oxides, entirely disappear before the distilling metals. In the case of the zinc, but little of the sulphide was carried into the cool portion of the tube lying beyond the furnace. The sulphide of cadmium was transported farther and in much larger quantities than the sulphide of zinc. In the cool portion of the tube beyond the furnace its crystals could be seen to form and fall in a manner resembling a fine rain. By rapidly raising the temperature the sulphide of cadmium may be made to dissociate with almost explosive violence. In this way, on several occasions when the sulphide and its metal were not so distributed behind the dam as to leave considerable free space between it and the top of the tube, the material was blown through the entire length of the tube into the pump.

The dissociation of the oxides appears to begin at a somewhat lower temperature than that of the sulphides. Of the two oxides, the oxide of zinc appears to dissociate the more readily; of the two sulphides, the sulphide of cadmium.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

THE ELECTROLYTIC SEPARATION OF CADMIUM FROM ZINC.

By Edgar F. Smith and Lee K. Frankel.

The separation of these metals has been effected by Yver,[1] who employed the acetates for this purpose. Eliasberg[2] and Smith and Knerr[3] confirmed this observation, at the same time emphasising the fact that the current should be carefully regulated, otherwise unsatisfactory results would be obtained. A solution, containing cadmium and zinc as tartrates together with free tartaric acid, will also yield all its cadmium to a current generating 0.4–0.5 cc. oxy-hydrogen gas per minute.[4] We have no record of other salts of these metals having been used for their electrolytic separation, and therefore have taken occasion to learn what might be the result with solutions of the double cyanides, such as we employed in separating mercury and copper.[5]

Beilstein and Jawein[6] have shown that both cadmium and zinc can be completely precipitated from a cyanide solution, but have not given the current strength employed by them in their experiments, nor did they attempt the separation of these metals from each other.

As our experience with mercury and copper clearly indicates, it is frequently possible by close attention to the current to effect electrolytic separations which ordinarily seem impossible. With this fact clearly before us, our first work, with the metals now under consideration, was to ascertain how feeble a current would suffice for the complete deposition of each metal, when alone in a cyanide solution, in the presence of an excess of an alkaline cyanide. We very soon discovered that the cadmium separated readily and with a much weaker current than was necessary for the deposition of the zinc. The latter will, however, separate from a cyanide solution, even under the influence of a feeble current, but not until the excess of cyanide has been completely decomposed. With the quantity of cyanide used by us, and with a current of the strength indicated below, this complete decomposition of the alkaline cyanide is not

[1] Bull. Soc. Chim. de Paris **34**, 18.
[2] Ztschr. anal. Chem. **24**, 548.
[3] This Journal **8**, 210.
[4] This Journal **8**, 210.
[5] Journal Franklin Institute **127**, 469, and this Journal **11**, 264.
[6] Ber. d. chem. Ges. **12**, 446, 762.

likely to occur in a shorter period than forty-eight hours. Hence it follows, that as the quantity of cadmium used in our experiments is entirely precipitated in a little more than eighteen hours, the complete separation of cadmium from zinc is thoroughly feasible by this method.

All our experiments were conducted in the cold, and care was taken in each case to examine the deposited metal for zinc, and the residual solution for cadmium. The conditions under which our work was carried out and the results obtained are these:

Metallic Cadmium in grams.	Cadmium Found.	Metallic Zinc present.	Difference in per cent. of Cadmium.	KCN in grams.	Total Dilution.	Current in cc. of O = H Gas.	Time.
.1817	.1813	...	—.22	4.5 grams in each separation.	200 cc.	.3 cc in each experiment.	18–23 hours.
	.1818	...	+.05				
	.1815	...	—.11				
	.1822	..	+.22				
	.1812	.2000	—.27				
	.1818	"	+.05				
	.1828	"	+.60				
.2426	.2422	...	—.16				
	.2432	...	+.24				
	.2426	...	...				
	.2420	.2000	—.24				
	.2435	"	+.30				
	.2429	"	+.12				
	.2426	"	...				
	.2433	"	+.28				
	.2434	"	+.32				

The cadmium deposit was light gray in color and crystalline in structure. It was washed with hot water and dried upon a warm iron plate.

CHEMICAL LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, PA., *May* 21, 1889.

OF THE SOLUBILITY OF THE CONSTITUENTS OF SEEDS IN PREPARED SOLUTIONS OF PTYALIN, PEPSIN AND TRYPSIN.

By W. Maxwell.

Supplementary to a study of the constitution of the legumes—Pisum sativum, Faba vulgaris, and Vicia sativa—experiments were conducted by the author in the Agricultural-Chemical Laboratory of the Zürich Polytechnic, by way of approaching a knowledge of the action of the animal solvents upon the several groups of plant constituents, and of the total solubility of each respective seed.

The investigations were pursued according to a generalisation of the methods adopted by Prof. Stutzer[1] in his valuable studies on artificial digestion.

Prof. Stutzer found that the mean of solubility of the nitrogenous constituents of vegetable substances was obtained by the consecutive treatment of the substance with solutions of gastric juice (pepsin) and pancreatie juice (trypsin).

The mean digestibility of the non-nitrogenous matters is consequent upon treatment with ptyalin (diastase solution may replace ptyalin),[2] pepsin and trypsin in the natural order in which these solvents operate in the animal system.

These experiments were conducted as follows: A considerable quantity of material (50–100 grams) was treated with a solution of diastase until wholly free from starch and the substance gave no further color reaction with iodine. The residue was thoroughly washed out, dried, and weighed.

Of the diastase residue, a given weight (about 2 grams) was treated with a solution of pepsin. The undissolved residue was washed out, dried, and weighed. The nitrogen remaining in the pepsin residue was determined according to the method of Kjeldahl.

A second quantity of the diastase residue was digested consecutively with solutions of pepsin and trypsin, and the undissolved residue treated precisely the same as the pepsin residue.

The pepsin solution was prepared according to the notes of Stutzer, and the solution of trypsin as given by Haidenhain.[3] The estimations are calculated upon material dried at 100° C.

[1] Ztschr. phys. Chem. **12**, Heft I, II, 1887.
[2] Ibid.
[3] Pflügers Archiv **10**, S. 582 und 576.

Pisum sativum.

		Dissolved.
Original material	64.43 grams.	
(1) After treatment with diastase.....	25.50	58.87 per cent.
(2) After further treatment with pepsin.....	9.47	24.87
(3) After further treatment with trypsin.....	7.30	5.99
Total solubility.....		89.73

The original material contained 4.151 per cent. of nitrogen. After digesting the diastase residue with pepsin, the undissolved nitrogen in the residue, in proportion to the total nitrogen, was 0.143 per cent. The second quantity of diastase residue, which had been digested with pepsin and trypsin consecutively, a nitrogen determination of the final residue yielded only 0.091 per cent. Solubility of the total nitrogen = 97.77 per cent.

The solubility of the nitrogenous bodies we are not able, with even approximate certainty, to deduce from the percentage of the total nitrogen dissolved. The nitrogen in vegetable organisms is distributed in combinations, certain of which the molecular structure and value is not known. If, however, in order to form, for the present, an approximate judgment of the comparative solubilities of the nitrogenous and non-nitrogenous constituents, we consider the nitrogen dissolved as expressing the amount of the soluble nitrogenous bodies, the solubility of the non-nitrogenous substances may be calculated by difference, and in the example of Pisum sativum the amount was found to be 91.95 per cent.

The undissolved residue of the seed appears as follows:

Insoluble nitrogenous matter.....	2.22 per cent.
Insoluble non-nitrogenous matter...	8.05
	10.27

Faba vulgaris.

		Dissolved.
Original material	80.04 grams.	
(1) After treatment with diastase.....	34.10	57.39 per cent.
(2) After treatment with pepsin.....	11.89	24.77
(3) After treatment with trypsin.....	10.36	3.65
Total solubility.....		85.81

	Dissolved.
Total nitrogen contained in original material..	4.477 per cent.
After digesting the diastase residue with pepsin	0.239
After digesting the diastase residue with pepsin and trypsin	0.160
Solubility of total nitrogen—nitrogenous bodies (?)	96.43 per cent.
Solubility of non-nitrogenous bodies	89.38
Insoluble nitrogenous matter	3.57 per cent.
Insoluble non-nitrogenous matter	10.62
	14.19

Vicia sativa.

Original material	90.94 grams.	
(1) After treatment with diastase	39.80	56.23 per cent.
(2) After treatment with pepsin	13.41	28.96
(3) After treatment with trypsin	11.59	2.04
Total solubility		87.23
Total nitrogen in the original material		5.039 per cent.
After digesting the diastase residue with pepsin		0.291
After digesting the diastase residue with pepsin and trypsin		0.255
Solubility of total nitrogen—nitrogenous bodies (?)		94.95 per cent.
Solubility of non-nitrogenous bodies		92.26
Insoluble nitrogenous matter		5.03 per cent.
Insoluble non-nitrogenous matter		7.74
		12.77

An experiment was made in order to observe the digesting effect of pepsin by direct treatment of the original material. It was found, in the example of Faba vulgaris, that only some 32 per cent. of the total seed-matter was dissolved, of which 25.23 per cent. consisted of the albuminoids. The result was so remarkable that some doubt appeared to be involved, and a nitrogen determination of the residue was made in order to be sure that the solvent had been operative.

Nitrogen contained in the residue	0.240 per cent.
Previous nitrogen contained in pepsin residue of the same seed	0.239

It appears from these experiments that the starch contained in the seeds not only remains undissolved, it also exercises a preventive effect upon the digestion of the other insoluble carbohydrates (paragalactine, etc.). This observation is in support of Stutzer's sequence of solvents by which the mean solubility of the non-nitrogenous substances is effected.

It is of interest to observe from the above tables the action of pancreatic juice upon the nuclein bodies which had been liberated from their albuminoid combinations (nuclein albumines) by the preceding digestion with pepsin. These bodies (nucleins), which remained intact under the protracted action of the acid pepsin solution, yielded up a considerable portion of their nitrogen to digesting with an alkali solution of trypsin.

It may here be in place to call attention to a general error attaching to the estimation of albuminoids by means of the common methods. The "nucleins" are insoluble in water, consequently they are not removed with the soluble nitrogenous compounds, but are contained in the albuminoid precipitates and necessarily in the nitrogen determination. Where the error has not been allowed, in more strictly scientific studies, the albuminoid estimations will be found too high, and in proportion to the amounts of nucleins present.

The results obtained by artificial methods of digestion, and the data gathered from trials with living animals, indicate such a measure of agreement as to confirm the value of laboratory experiment. In certain cases living tests have given higher results than artificial experiment. The contrary is, however, the more general, or the rule. And this fact has been understood from the consideration that larger amounts of food-matters are served to animals than the juices of the system are capable of reducing to the absolute degree of solubility. Proofs of this occur frequently in the instances of animals (pigs and fattening cattle) which are being fed with a very concentrated diet. In examples where animal digestion has given higher results than artificial experiment, the results have been considered in relation to the supplementary action of micro-organisms in digestion processes. The investigations conducted by Stutzer artificially, and by Prof. Pfeiffer with living animals, are valuable contributions to this subject.[1]

HARVARD COLLEGE LABORATORY.

[1] Ztschr. phys. Chem. **9**, 213.

NOTES.

On Allotropic Forms of Silver.

M. Carey Lea has just given an account of three allotropic forms of silver. The following quotations from the original article[1] will give a general idea of the character of his results:

"Silver is capable of existing in allotropic forms possessing qualities differing greatly from those of normal silver. There are three such forms, or rather three modifications of one form, differing from each other in many respects, but all more nearly related to each other than any one of them to normal silver. One of these forms is soluble in water, passing readily to an insoluble form, and this last may, by the simple presence of a neutral substance exercising no chemical action upon it, recover its solubility. Another form closely resembles gold in color and lustre. . . . These allotropic forms of silver are broadly distinguished from normal silver by color, by properties, and by chemical reactions. They not improbably represent a more active condition of silver, of which common or normal silver may be a polymerised form. Something analogous has already been observed with other metals, lead and copper. . . . . The forms of allotropic silver which I have obtained may be classified as follows:

"*A.* Soluble, deep red in solution, mat lilac, blue, or green whilst moist, brilliant bluish green metallic when dry.

"*B.* Insoluble, derived from A, dark reddish brown while moist, when dry somewhat resembling A.

"*C.* Gold silver, dark bronze whilst wet, when dry exactly resembling metallic gold in burnished lumps. Of this form there is a variety which is copper-colored. Insoluble in water, appears to have no corresponding soluble form.

". . . All these forms have several remarkable properties in common:

"1. *That of drying with their particles in optical contact, and consequently forming a continuous film.*—If either is taken in a pasty condition and is spread evenly over paper with a fine brush, it takes on spontaneously in drying a lustre as high as that of metallic leaf. C, when so treated, would be taken for gold leaf. But this property is much better seen by brushing the substance over glass. When dry, an absolutely perfect mirror is obtained. The particles next the glass, seen through the glass, are as perfectly continuous as those of a mercurial amalgam, and the mirror is good. A and B form bluish-green mirrors, C gold or copper-colored mirrors.

[1] American Journal of Science **37**, 476 (1889).

"2. *The halogen reaction.*—When any of these allotropic forms of silver are brushed over paper and the resulting metallic films are exposed to the action of any haloid in solution, very beautiful colorations are obtained. . . . . With sodium hypochlorite the colors are often magnificent, intense shades with metallic reflections, reminding one of the colors of a peacock's tail. . . .

"3. *The action of acids.*—The stronger acids, even when much diluted, instantly convert the allotropic forms of silver into normal gray silver; even acetic acid, not too much diluted, does this.

"4. *Physical condition.*—All these allotropic forms of silver are easily reduced to an impalpable powder. One is surprised to see what is apparently solid burnished metal break easily to pieces and by moderate trituration yield a fine powder."

When dilute solutions of ferrous citrate and of a silver salt are brought together a deep red liquid is formed. If the solutions are concentrated the liquid turns almost completely black. In the latter case a precipitate of a fine lilac-blue color is formed. This precipitate is insoluble in several saline solutions, but it dissolves easily in pure water with an intense red color. Analysis of this precipitate showed that it contained 97.27 per cent. of silver and no hydrogen nor oxygen, the remaining 2 or 3 per cent. being fully accounted for by ferric oxide and citric acid present as impurities. The solution formed in water was examined optically and found to be a true solution. The substance, when treated with mercury, amalgamates by simple friction. The author says: "If I had been able to find any other explanation for these facts without admitting the solubility of silver, I should have adopted it. But none presented itself."

The insoluble form B is obtained by adding certain neutral salts to the solution of the soluble form A above described. Among the salts which may be used for this purpose are magnesium sulphate, cupric sulphate, ferrous sulphate, etc. The insoluble form is purple brown, and "by repeated washing, by decantation or otherwise, continually darkens." It is curious "that the insoluble form may be made to return to the soluble condition. Many substances are capable of effecting this change. Sodium borate does so, producing a brown solution; potassium and sodium sulphate produce a yellowish red solution, and ammonium sulphate a red one. None of these solutions has the same blood-red color as the original solution; the form of silver seems to change with the slightest change of condition." The analysis of this substance showed that it contained 97.96 per cent. of silver, and that the remaining 2.04 per cent. consisted of ferric oxide and citric acid.

The gold-yellow and copper-colored silver (C) is obtained in the following way: "Two mixtures are to be prepared: No. 1, containing 200 cc. of a ten per cent. solution of silver nitrate, 200 cc. of a twenty per cent. solution of Rochelle salt, and 800 cc. of distilled water. No. 2, containing 107 cc. of a thirty per cent. solu-

tion of ferrous sulphate, 200 cc. of a twenty per cent. solution of Rochelle salt, and 800 cc. of distilled water. The second solution (which must be mixed immediately before using only) is poured into the first with constant stirring. A powder, at first glittering red, then changing to black, falls, which in the filter has a beautiful bronze appearance. After washing it should be removed whilst in a pasty condition and spread over watch-glasses or flat basins and allowed to dry spontaneously. It will be seen that this is a reduction of silver tartrate by ferrous tartrate. . . . Although the gold-colored silver (into which the nitrate used is wholly converted) is very permanent when dry, it is less so when wet. In washing, the filter must be kept always full of water; this is essential. It dries into lumps exactly resembling highly polished gold, especially the surfaces that have dried in contact with glass or porcelain. . . . When the thick pasty substance is extended over glazed paper, it dries with the splendid lustre of gold leaf, with this essential difference, that these allotropic forms of silver B and C assume spontaneously in drying the high degree of brilliancy which other metallic surfaces acquire by elaborate polishing and burnishing. By brushing a thick paste of this substance evenly over clear glass, beautiful gold-colored mirrors are obtained. The film seems to be entirely continuous."

The analysis of the gold-colored variety showed that it contained 98.75 per cent. silver, and that the residue was almost wholly ferric tartrate. I. R.

Determination of Iron in the presence of Hydrochloric Acid by means of Permanganate of Potassium.

In 1884, C. Reinhardt published an account of a method for the determination of iron which consisted of the following operations: 1st, reduction of the hot ferric chloride by means of stannous chloride; 2d, conversion of the excess of stannous chloride into stannic chloride by means of mercuric chloride; 3d, addition of manganese sulphate to the greatly diluted solution; 4th, titration with permanganate.

The solution becomes yellow in consequence of the formation of ferric chloride; and finally, when the oxidation is complete, it changes to a brown instead of a rose color. The detection of the end of the reaction is thus rendered somewhat difficult. But Reinhardt finds that this difficulty may be wholly avoided by the addition of phosphoric acid. The solution then remains colorless, and the completion of the oxidation is indicated by the appearance of the pure rose-color.

The solutions employed are:

1st. 6 grams of permanganate dissolved in 1000 cc. of water and standardised by tetraoxalate of potassium.

2d. 200 grams of manganese sulphate dissolved in 1000 cc. of

water to which a few cubic centimeters of diluted sulphuric acid have been added; 1000 cc. phosphoric acid, specific gravity 1.3, diluted with 600 cc. of water and carefully mixed with 400 cc. of sulphuric acid, specific gravity 1.8. The manganese sulphate and phosphoric acid solutions, when the latter has cooled down, are mixed together. Amount required for a single determination, 60 cc.

3d. 50 grams of mercuric chloride dissolved in 1000 cc. of water. Amount required for a single determination, 60 cc.

4th. 120 grams of tin free from iron dissolved in 500 cc. of hydrochloric acid, specific gravity 1.19. After allowing the hydrochloric acid and tin to act for some time in the cold, the solution is completed by warming on the water-bath. The solution is then diluted to 1000 cc. with water, and filtered through asbestus free from iron into a mixture consisting of 2000 cc. of water and 1000 cc. of hydrochloric acid, specific gravity 1.124. Each cubic centimeter is equivalent to 0.020 gram of iron.

0.5 to 1.0 gram of the material previously roasted, if necessary to oxidise sulphur, carbon or organic matter, is dissolved with heat in 25–30 cc. of hydrochloric acid, specific gravity 1.19. This solution is treated with the solution of stannous chloride until it becomes colorless, then with 60 cc. of the solution of mercuric chloride. Its volume is finally increased to 1500 cc. by the addition of water faintly reddened with permanganate and containing 60 cc. of the solution of manganese sulphate and phosphoric acid. In this way a sharply defined end-reaction is obtained.

The quantity of permanganate required to redden the water employed in diluting to 1500 cc. is subtracted, in calculating the results, from the total quantity of permanganate used.—(*Chem. Zeit.* **13**, 323.)

G. A. Krauss.

ERRATUM.

Page 488 (Vol. X, No. 6). In the second part of the table beginning with "Bread," the column headed "Fat" should have been headed "Nitrogen-free extract," and *vice versa*.

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F. W. C.